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THE DESIGN OF A MASS SPECTROMETER
FOR THE ANALYSIS OF HYDROGEN ISOTOPES

BY

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A THESIS

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled "THE DESIGN OF A MASS SPECTROMETER FOR THE ANALYSIS OF HYDROGEN ISOTOPES", submitted by Leo Patrick Buckley in partial fulfilment of the requirements for the degree of Master of Science in Chemical Engineering.

ABSTRACT

The study of systems involving the isotopic exchange of hydrogen and deuterium has prompted the construction of a special mass spectrometer within the Department of Chemical and Petroleum Engineering for the analysis of hydrogen isotopes.

Review of the literature showed mass spectrometry to be the most precise method for the analysis of deuterium at its natural abundance level. The mass spectrometer, a 90° sector analyzer with a radius of 2.5 inches, was constructed of stainless steel. The instrument employs simultaneous dual collection of the isotopes and the source utilizes a repeller which is effective in reducing the H_3^+ ion production. The mass spectrometer uses a permanent magnet having a field strength of 1850 gauss. Scanning of the various peaks is accomplished by changing the accelerating potential with time.

The detection of deuterium requires that the sample enter the source of the instrument as hydrogen gas. To make the instrument more versatile, and to broaden the range of samples that can be analyzed, a uranium furnace has been incorporated in the design. The uranium can reduce simple hydrogen containing compounds such as water, hydrogen sulphide and ammonia to hydrogen gas for direct analysis.

A procedure for determining deuterium concentration by comparing to reference standards is demonstrated. The time required to obtain ion current ratios for an individual sample is approximately ten minutes. The precision of analysis is ± 6 ppm in the range of 100 - 200 ppm of deuterium.

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CHAPTER I

INTRODUCTION

Isotopes are atoms of the same element, which because of their different masses exhibit different physical and chemical properties. Deuterium, the isotope of hydrogen, having mass two is a significant species. It was discovered by Urey and co-workers (1) in 1931. A number of deuterium species will be present in any hydrogen-containing compound, for example, water contains H_2O , HDO and D_2O . At natural abundance levels in water, deuterium is present mostly as the compound HDO . Significant amounts of D_2O can only be obtained by concentration of the deuterium. Heavy water, D_2O , is used as a coolant and moderator in Canadian designed nuclear power reactors. The natural abundance of deuterium is one atom per 6500 atoms of hydrogen and the principle sources of deuterium are water and natural gas.

In isotope pairs the physical differences arising from the difference in mass are not as pronounced as that found for hydrogen and deuterium. These differences lead to many isotope effects. For example, the natural abundance of deuterium in water varies with geographical location because of the preferential evaporation of the lighter isotopic species. These natural isotope fractionations have lead to deuterium concentrations in ocean waters which are higher than those found in fresh waters.

Hydrogen and deuterium also differ significantly in chemical reactivity, and these differences lead to equilibrium constants that are different from one for isotopic exchange reactions such as



Equilibrium exchange reactions form the basis of processes used for the concentration of deuterium and hence the ultimate production of heavy water. Information on the separation factors and kinetic rate constants for the exchange reactions is required when designing heavy water recovery processes.

Isotope studies have played an important role in the study of mechanisms of chemical reactions and in the development of theories of rate processes. In competing isotope reactions significant kinetic isotope effects will only take place if the bond associated with the isotopic atom is broken in the rate determining step. Rate processes, such as water evaporating through a thin film, can be studied by measuring the change of the deuterium concentrations with time and the information may be of use to determine the rate controlling mechanism.

Abundance measurements, studies of kinetic isotope effects and the measurement of separation factors and kinetic rate constants require a method of analysis for deuterium at low concentration. The mass spectrometer has been shown to be the most reliable instrument available. It is capable of good resolution of the isotopes of hydrogen and has demonstrated a reliable performance record of analysis. However, commercial machines which have the necessary resolution are expensive and it is preferable to have an instrument that is only used for hydrogen isotope analysis. Thus a decision was made to build a precision instrument which would be used at the University of Alberta only for hydrogen isotope analyses.

This thesis describes the design and construction of the instrument and presents an analysis of its performance.

CHAPTER II

ANALYTICAL METHODS FOR THE ISOTOPIC ANALYSIS OF HYDROGEN

The following is a brief review of the various analytical techniques which may have application for the analysis of low isotopic concentrations of hydrogen in simple hydrogen-containing compounds. In evaluating the various methods one should consider the following salient factors: accuracy, reliability, rapidity of analysis, ease of operation, and the maintenance required.

2.1 Spectroscopic Method

The first quantitative estimation of deuterium was carried out by the spectroscopic method of Urey, Brickwedde and Murphy (1). The measurement was based on the different wave lengths of the corresponding lines in the atomic spectra of light and heavy hydrogen. The concentration ratio of the isotopes was assumed to be equal to the reciprocal of the times of exposure required to give spectrum lines of equal intensity. The analysis of a particular sample gave equal intensities for the two species only after the deuterium had been exposed for more than one hour compared to hydrogen's exposure time of one second indicating that the ratio of deuterium to hydrogen was 1:4500.

The spectroscopic method has limitations. The photographic emulsions used are extremely light sensitive and any discharge hitting the surface will not give completely defining lines. A mass spectrophotometer that has a dispersion in the range of one Angström per millimeter, i.e. very high quality, will allow for low concentrations of the gas to be measured on an absolute basis.

2.2 Infrared Spectrometry

Several laboratories became interested in infrared spectrophotometry as a method of analysis for heavy water as early as 1950. The method promised advantages in speed, simplicity and precision. Early procedures were severely limited in the ranges of concentration that could be analyzed. Gaunt (2) and others (3) reported methods for concentrations greater than 99.6% D₂O and less than 0.8% D₂O with precisions of $\pm 0.005\%$ in the upper range. In 1954 Stevens and Thurston (4) developed a method which is applicable over greater ranges whereby samples were diluted with natural water or high grade D₂O to bring them within the ranges of their instrument. Later work (5) incorporated a neutral, variable filter for the reference beam and a method of measuring "transmission" peaks rather than "absorption" peaks. The precision attainable in the natural concentration level was limited to ± 0.003 atom % D., because temperature changes had a large effect on extinction coefficients for H₂O.

Further work by Thurston et al (6) employed rapid changing of the cells of reference and unknown waters and the use of interference filters. These changes increased the precision to ± 2 ppm of deuterium which is essentially ± 0.0002 at % D.

The infrared technique requires very pure water samples and the deuterium in simple hydrogen compounds can only be determined by combusting to water or exchanging the deuterium with water. Burning simple compounds of hydrogen like amines will dilute the exchangeable hydrogens with the non-exchangeable hydrogen atoms associated with the carbon atoms. Also, during the combustion process the water sample can be contaminated with other oxides of combustion, for example,

oxides of nitrogen.

This problem might be overcome by exchanging the deuterium of these simple hydrogen compounds with hydrogen atoms of water having a known isotopic composition. The drawback is prior knowledge of the separation factor of the exchange reaction. Once this is obtained, analyzing the water will then give the deuterium content of the compound under analysis.

2.3 Mass Spectrometry

Bleakney (7, 8) was the first to apply mass spectrometry to the analysis of deuterium. In this method, a small amount of hydrogen gas is ionized in a high vacuum and the ions of mass two are separated from those of mass three by means of suitable magnetic and electric fields.

Kirshenbaum (9) describes methods used in 1950 and reports a precision of ± 0.0005 at % D for naturally occurring concentrations of deuterium. Later mass spectrometer measurements of the deuterium content in natural waters were reported by Dansgaard (10), Friedman (11), Horibe and Kobayakawa (12). Using improved techniques, precision was attainable to ± 0.0002 at % D.

Recent developments in mass spectrometer techniques for analyzing deuterium include those of Nief and Botter (13), Murthy and Rao (14) and Bigl (15). Since the mass spectrometer requires hydrogen and deuterium to be present as hydrogen gas, a uranium furnace was incorporated by Nief and Botter to decompose simple hydrogen compounds and release the hydrogen gas directly into the mass spectrometer. With the use of the furnace, the time required

for the analysis per sample was from five to ten minutes. Less risk of contamination in using an all-metal inlet system and mass spectrometer was the feature of design of Murthy and Rao. Bigl utilized a 180° machine where the source was within the magnetic field of the analyzer. He reported low production of H_3^+ through his use of improved source design. Problems of contamination and dilution of the hydrogen atoms in converting them to the gaseous state are still present, but Nief and Botter and Bigl were able to analyze samples to better than 0.2 ppma D. or 0.00002 at % D.

2.4 Thermoconductivity Method

The micro-thermoconductivity method for the determination of ortho and para hydrogen was applied by Farkas and Farkas (16,17) to estimate the deuterium concentration in hydrogen. The apparatus has to be calibrated using samples of hydrogen containing known amounts of the heavy isotope. The method has a claimed accuracy of $\pm 0.1\%$ and can be used only if the deuterium content is not too low, that is, not less than 1%. The amount of gas required is about two or three cubic millimeters at standard conditions per measurement. For analysis of other than hydrogen gas requires similar reduction apparatus previously mentioned.

2.5 Gas Chromatographic Method

The use of gas chromatography for the quantitative separation of isotopes of hydrogen was reported by Glueckauf and Kitt (18). This work stimulated efforts to find a suitable adsorbent to enable chromatography to be used as an alternative to mass spectrographic methods for the determination of hydrogen isotopes.

Smith and Hunt (19) reported a chromia-alumina column operated at 77°K with neon as the carrier gas that separated hydrogen into its isotopes. Subsequently Moore and Ward (20), Shipman (21), and Furuyama and Kwan (22) have shown that good isotopic separation results with helium as the carrier gas on columns of alumina coated with ferric oxide. However, for low concentrations the quantitative determination of hydrogen is difficult for several reasons. Sensitivity is low, because there are small differences in the thermal conductivities between hydrogen and helium. Furthermore, hydrogen-helium mixtures elicit anomalous responses from thermal conductivity cells in some concentration ranges. When the percentage of hydrogen in helium is high, the response is as anticipated, but at low hydrogen concentrations the detector behaves as if hydrogen had a lower rather than higher thermal conductivity and the result is an inversion in the peak.

Moore and Ward (20) used CuO in their column to convert the hydrogen to water. Helium-water has a higher thermal conductivity difference than helium-hydrogen, however, isotope separation is more difficult. The length of time in running a few millilitres of gas samples varied from 133 minutes (19) to 8 minutes (23). The accuracy obtained by Moore and Ward (20) suggested that deuterium can be detected in hydrogen as HD as low as 0.01% of the hydrogen peak present. This resolution is satisfactory for locating exchangeable hydrogens on carbon chains, but not for natural hydrogen isotope studies. Gas or liquid samples can be used with this method.

2.6 Specific Gravity Method

For many years the variation of the specific gravity of water was the most important and most widely used method for the estimation of deuterium content (9). The float method of measurement is performed by varying either the temperature of the water or the pressure above it until the float neither sinks nor rises. The float method requires a calibration with solutions of known specific gravity, but the sample size required is only of the order of a few milligrams. In purifying samples by distillation for the float method, the liquid will become richer in deuterium and this may lead to erroneous results. Values of precision of $\pm .0005$ mole % have been reported (24,25). Again, as in the thermoconductivity method, the problem of obtaining calibrated standards arises.

2.7 Other Methods

In general, the difference in any property of light and heavy water or protium and deuterium may be utilized for the determination of deuterium content, provided the difference is large enough to be measured conveniently. Such differences exist between the freezing points, viscosities, vapour pressure and refractive index. With these properties, however, temperature effects can be quite significant. In addition, the analysis of the isotopes using these properties requires the deuterium to be present in concentrations that are well beyond the level of the heavy isotope in natural occurring abundances.

CHAPTER III

MASS SPECTROMETRY3.1 Historical Introduction

The forerunner of all mass spectrometers was built by J. J. Thomson (26) in 1910 with which he separated different mass components of the element neon. A beam of positive ions from a gas discharge tube passed through a long narrow channel and then was projected into a mass analyzer. This collimated beam was subjected to the combined action of parallel electric and magnetic fields. The deflection of the beam was at right angles and the ions impinged on a fluorescent screen. This arrangement set ions of a given mass to charge ratio to fall on points along a segment of a parabolic path. The length of each parabola was due to the differences in the velocities of the ions created from the discharge. Those ions having different mass to charge ratios fell on different parabolas. If all the ions of the same mass to charge ratio had the same velocity point images would result. With this instrument Thomson was able to detect two types of atoms of neon one of relative mass weight twenty-two, the other of relative mass weight twenty.

In 1919 Aston (27,28) extended the work of Thomson and produced a new type of positive ray apparatus that gave a spectrum of lines each corresponding to a certain mass to charge ratio. The principle behind his apparatus was that the ions were deflected in turn by an electric and magnetic field. Even though ions of the same mass to charge ratio enter the mass analyzer with a large range

of velocities and follow different paths, they converge to a line image at the surface of a photographic plate. This action is known as velocity focusing. Aston, with this machine, was capable of distinguishing mass to charge ratios differing as little as one part in one hundred thirty and was able to contribute much to the knowledge of isotopes.

Dempster (29) at the same time carried on a search for isotopes using an entirely different design. His apparatus, the first true mass spectrometer, produced ions by bombarding a gaseous substance with electrons of low kinetic energy. These ions were electrically accelerated and then acted upon by a transverse magnetic field. Later, Bainbridge (30) improved the mass spectrometer by combining the designs of Aston and Dempster.

This then lead to two distinct fields of study. One, the accurate determination of isotopic mass with improved designs by Aston, Dempster, Bainbridge and Jordan, Mattauch, and others. It has become known as mass spectrophotometry mainly because the measurements are made with ion sensitive photographic emulsions. The other, measurement of the relative abundance of different mass components of an element or of a mixture of elements or compounds. The technical advances leading to more reliable instruments were carried on by Bleakney (7), Tate and Smith (31) and by A. O. C. Nier (32,33,34) particularly.

3.2 Mass Spectrometer Systems

A mass spectrometer can be considered as a system where interacting elements of assembled equipment carry out, cooperatively,

the functions of obtaining the relative intensities of various species in the sample and the identification of these species by their mass to charge ratio. The system consists of a number of elements and each must be treated separately by specifying the input it receives, the process it performs and the output it generates.

Each mass spectrometer, regardless of what its special design, is comprised of four function elements: one, the source, where a beam of ions representative of the sample under investigation is generated; two, the analyzer, in which the separation is effected either in space or time; three, the detector, where the resolved ions are detected and their intensity is measured; and four, the vacuum system, which provides the environment for these processes. The sample inlet systems and recorders are subsystems of the vacuum and detector systems respectively. These features are shown in Figure 3.1.

The most important method of producing ions is to collide neutral atoms or molecules and energetic electrons at low pressures in electron bombardment sources. Almost all organic spectrometry is carried out with such sources. Two other types in the field of study of organic compounds are: field emission sources where ionization is achieved by strong electrical fields; and photoionization sources where ultraviolet light of sufficient wave length is employed. Inorganic solids are analyzed in either a thermal ionization source where ionization takes place during evaporation from a heated metal surface or in a vacuum discharge source where ions are formed in sparks or arcs.

Mass analyzers are classified into two broad groups. The static type analyzers utilize the momentum dispersion properties of

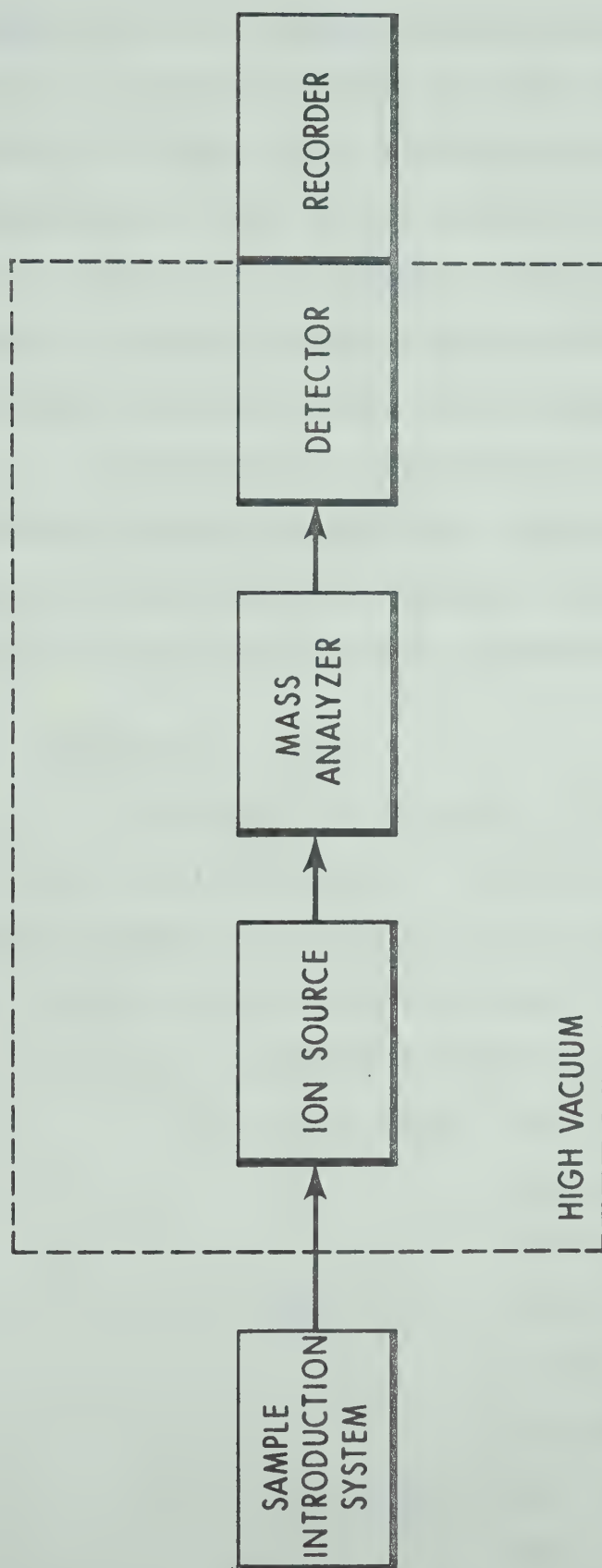


Figure 3.1 THE DIAGRAM OF A MASS SPECTROMETER SYSTEM (35)

magnetic fields and the energy dispersion properties of electric fields in such a way that the instrument parameters are kept constant in time. The dynamic type instrument employs time dependence of a parameter as the basis of mass separation. The differences in the time of flight of ions in evacuated tubes, the time dispersion properties of the radio frequency field and other properties are utilized in addition to those already mentioned for the static types.

Ion detectors are based either on the conversion of the individual separate ion beams into a proportional electron current which can be amplified and recorded or on the simultaneous collection of all ion beams using ion sensitive photo emulsions.

3.3 Ion Sources

The choice of an ion source is dictated by the nature of the sample being investigated. The functions of an ion source are to produce as many ions as possible from the neutral particles present and to form, shape and eject an ion beam that is suitable for entrance to an analyzer. The following factors must be considered:

- (i) energy spread - the difference in the amount of energy across the width of the ion beam.
- (ii) sensitivity - ratio of ions produced per neutral sample atom or molecule introduced.
- (iii) ion species produced - mostly singly charged species to get maximum sensitivity and minimum interference.

- (iv) background & memory - ions produced which do not originate in the sample must be kept to a minimum by good vacuum techniques which also reduce cross contamination between samples.
- (v) mass discrimination - electric and magnetic fields of the source do not behave the same for ions of different masses.
- (vi) ion current stability and noise - ability to keep ion current well regulated means more reproducible results.

There are many types of ion sources of which the following are the most important: electron bombardment, surface ionization arcs, vacuum spark, ion impact and field emission. The discussion here will be limited to electron bombardment because of the interest only in gas analysis.

The production of positive ions by electron input is a universally employed technique for gaseous compounds. With a suitably designed source one can produce a copious beam of ions having a reasonably small energy spread. No other source provides a comparable stability in ion production. The kinetic energy of the bombarding electrons can be varied, thus controlling the ionization of a specific molecule. As its name implies, ion formation is based on the exchange of energy during collisions between neutral gas molecules and energetic electrons. The type of ions formed and their relative

amounts depend mainly on the chemical nature of the sample, and on the energy of the bombarding electrons. When the electron energy reaches a certain value characterized by the ionization potential, formation of ions commences. The efficiency of ionization increases with increasing electron energy (36).

The electron bombardment source always possesses the common elements of an electron producing filament and electron trap, high voltage electrodes for accelerating the positive ions generated by electron impact and collimating slits to provide beam definition. A more complex source provides additional focusing electrodes. Most present day structures are based on a design by Nier (37).

The sample to be investigated is introduced in gaseous form into an evacuated chamber. Electrons are obtained by thermionic emission from a heated filament. The emitted electrons are collimated and accelerated through slits and enter the ionization chamber or case with kinetic energy equivalent to the potential difference between the filament and case. The difference is adjustable with the most frequently used value of 70 volts. Three types of currents can be measured, the filament current, the case current and the trap current, the latter two constituting the emission current. The filament current heats the filament, the presence of this current indicates that the filament is working and the magnitude is often an indication of the age of the filament. Since electrons scatter in all directions from the filament, the emission current is representative of the total number of electrons emitted. The case current is composed of those electrons that deviate the most from the electron beam that is directed toward the anode or trap plate. The most

important current is the trap current, as it is the measure of the number of electrons available for ionization within the case.

Keeping other parameters constant, the number of positive ions formed is directly proportional to the trap current. Because of this, the trap current is normally maintained constant at a predetermined value by electronic regulation.

To obtain a beam of ions that has a small energy spread, the bombarding electron beam is kept as narrow as possible by collimating with small permanent magnets (50-300 Gauss). The usual source of electrons is a tungsten or rhenium filament heated in a vacuum. The normal tungsten filament has a life of six to ten months. The source of heat in the ion chamber is from the filament, radiation from which results in a temperature of about 200°C. Some sources, such as those used for analysis of carbon compounds, have a regulated temperature.

The formation, shaping and acceleration of the ion beam and its injection into the mass analyzer are accomplished by a number of plates and slits kept at various potentials. Almost every investigator has his own favoured variant. Potential conditions of these plates and slits must be selected by considering whether maximum resolution or highest beam sensitivity is desired. The ion acceleration is accomplished by providing a regulated power supply capable of a few thousand volts potential. Other plates will control intensity, act as collimators and provide a means of vertical displacement of the beam. Most ion species formed are predominately singly charged although carbon compounds are notorious for having doubly and triply charged species.

The positive ion beam current available is limited to about 10^{-4} amperes due to space-charge effects which result in interference. Gas interference must be kept below three percent for accurate analysis of mixtures. The maximum source pressure should not exceed 10^{-4} mm of mercury.

Mass discrimination (38) in the source may be caused by the collimating magnetic field of the electron beam. Lighter ions or ions of lower energy are deflected somewhat more than heavier ions or higher energized ions. A compromise is generally made between the use of a strong magnetic field for good electron beam collimation but with high mass discriminations, and a weaker magnetic field with poorer electron beam resolution but very low mass discrimination.

Ionized residual gases result in background spectra. Background spectra may be important and is a serious problem for those instruments used in trace analysis. Most residual gases are the result of electrons releasing atoms or molecules from the walls of the vacuum enclosure. Memory problems may be caused occasionally by decomposition products and compounds that are difficult to pump away. If these are deposited on the plates or slits they can cause beam distortion. If memory problems persist, it can usually be attributable to poor vacuum and it may be necessary to operate at even higher vacuum.

The normal amount of sample needed in routine analysis is of the order of one cubic centimeter at standard conditions. Smaller amounts can be handled and as few as 5×10^5 atoms of xenon have been analyzed (39). Precision achievable is usually ± 0.01 percent in isotopic abundance measurements and ± 0.1 mole percent in the analysis

of gas mixtures.

Electron impact sources have many advantages. High yield, good energy homogeneity and stable ion beam are combined with convenient sample handling and easy operation. They are the most reliable of ion sources and hundreds of variations have been employed in qualitative and quantitative analysis.

3.4 Mass Analyzers

The mass analyzer has two objectives: first, to resolve an ion beam of mass, m , from another beam of nearly the same mass, $m + \Delta m$; and second, to maximize the resolved ion intensities. In other words, the mass analyzer must have dispersive and focusing action respectively. Magnetic and electric fields may be thought to be playing the roles that prisms and lenses do in conventional optics.

The motion of a charged particle, in this case an ion, is governed by the basic properties of momentum, energy and velocity. The charged particle acquires its velocity, v , by falling through an electrostatic potential difference, V . The potential energy, eV must be the same as the kinetic energy of the particle after acceleration

$$\frac{1}{2} mv^2 = eV \quad (3.1)$$

The charged particle of mass m , having charge e , and velocity v , moves at right angles to a magnetic field of flux density B , and experiences a deflecting force F_B exerted on it such that

$$F_B = Bev \quad (3.2)$$

The orbit of the charged particle entering a uniform

magnetic field at right angles to the field will become a circle of radius r_m . The magnitude of the velocity is not affected by the field. The mass of the ion in the circular orbit is acted on by a centripetal force, F_C .

$$F_C = \frac{mv^2}{r_m} \quad (3.3)$$

If the particles of various masses and velocities are mon-energetic, that is, mv^2 is constant then the forces can be considered equal to maintain equilibrium such that a momentum spectrum is set up

$$mv = Ber_m \quad (3.4)$$

This momentum spectrum can be rearranged by combining eqn. 3.4 and 3.1 to eliminate the velocity, obtaining a mass spectrum

$$\frac{m}{e} = \frac{r_m^2 B^2}{2V} \quad (3.5)$$

The true form of the mass spectrometer equation is found after conversion to atomic mass units thereby giving the mass-to-charge ratio for a specific radius, field density and acceleration potential.

$$\frac{M}{e} = 4.83 \times 10^{-5} \frac{R^2 B^2}{V} \quad (3.6)$$

Depending on the type of ion source employed, there will always be a certain degree of inhomogeneity in both the initial direction and the energy of the ions as they enter the analyzer. Spherical or angular aberrations in the ion beam result from the fact

that the slits in the source are in reality of finite width, and thus an ideal line-like ribbon of ions is not obtained. Focusing is required to eliminate overlapping and to maximize resolved ion intensities. If all the ions in the beam have the same energy then only directional focusing is required. A general analysis of focusing theory was first published by Herzog (40) and similar papers on wedge shaped magnetic fields were written by Barber (41) and Stephens (42).

The most commonly employed deflection angles for ion beams in a magnetic field are 180° , 90° , 60° . The focusing of a divergent beam by deflection in a magnetic field is not perfect. For a 180° deflection angle, the error in focusing results in beam widening as seen in Figure 3.2. Two trajectories of the same ionized mass, having the same radius, r , but diverging by an angle α , gives an error in focusing equal to EC . AE can be found from geometry to equal $2r\cos\alpha$. Therefore EC will be $2r(1-\cos\alpha)$. Now when α is small, one is justified in employing only the first two terms of the Taylor series expansion of $\cos \alpha$ so that the error in focusing will be (43)

$$EC \approx r\alpha^2 \quad (3.7)$$

The above equation represents the amount the ion beam diverges from its source slit definition in travelling to the collector. The size of the collector slit width is generally made comparable to this divergent beam.

For sector instruments (magnetic deflection less than 180°) the distance from the source, l_1 , and collector, l_2 , to the effective edge of the magnet results in a symmetrical analyzer. The condition

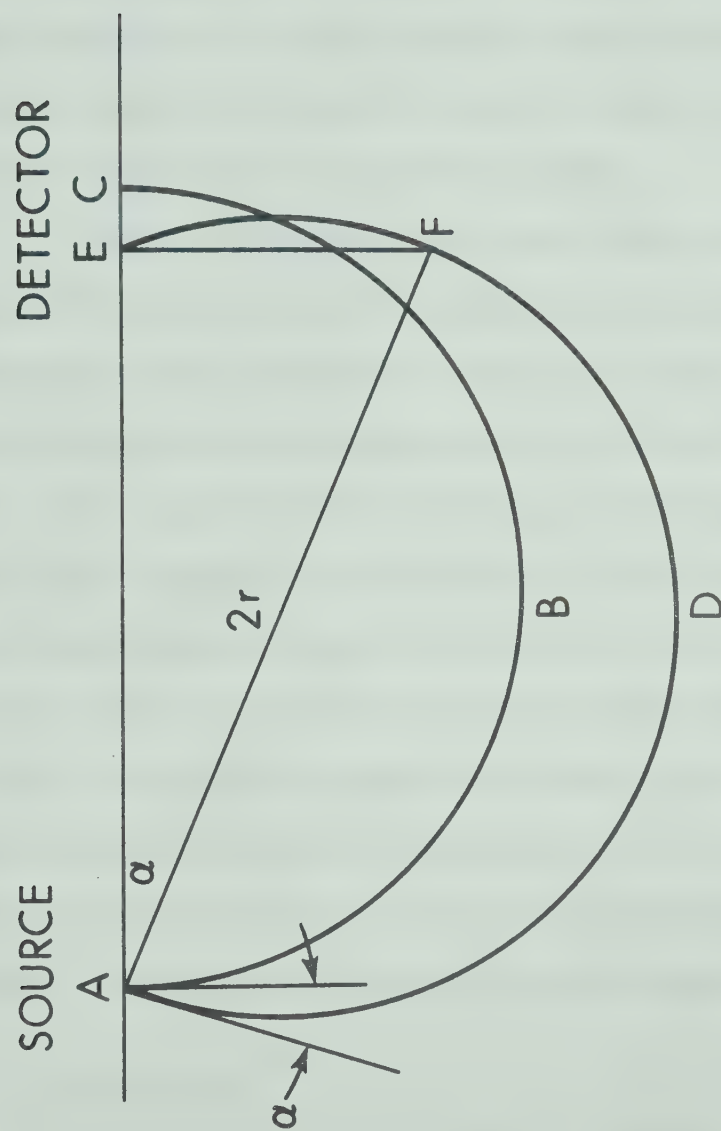


Figure 3.2 FOCUSING IMPERFECTIONS OF A DIVERGENT BEAM IN A 180° MASS ANALYZER

of focusing when the source and collector are in the same plane becomes (44)

$$l_1 = l_2 = r(\cot \phi + \csc \phi) \quad (3.8)$$

The correct location of the magnet can be ascertained from this expression where ϕ is the deflection angle of the magnet. The effective edge of the magnet is usually assumed to be the distance of the air gap from the edge of the magnet.

Reducing the deflection angle, reduces the area of the magnetic field for a given ion radius and so a smaller magnet is required for equal performance. At the same time, the gap width is reduced since the source and collector are both far from the magnetic field. Mass discrimination effects are also reduced. However, when using sector magnets, the ion beams must cross the magnetic field boundaries twice and since these boundaries are not sharp and well defined, a fringing field exists that distorts the beam trajectory. In sector instruments an additional magnet is required for collimating the electron beam in the source. The advantage then for the 180° type instrument lies in the construction of the source and analyzer within the field boundaries of the magnet.

3.5 Ion Detectors

Detection and measurement of positive ions sorted by the analyzer can be accomplished by electrical and photographic means. Electrical recording follows the variation of current with time, while a photoplate integrates the ion current. Sensitivity and speed of response are defining parameters, one of which can be increased

only at a sacrifice of the other. Electrical detection can be broken down into the processes of ion collection, amplification and recording.

The basic technique for detecting ion currents in the range of 10^{-6} to 10^{-13} amperes is to allow the beam to stop in a hollow conducting electrode. This type of beam monitor is often termed a "Faraday cage". A slit is used to give definition to a mass resolved ion beam and then the beam passes into a small cylinder that is electrically insulated from its surroundings. The slit edges are sharp enough to prevent ion reflection or scattering. The dimensions of the slit are chosen so that secondary electrons generated by the stopping of the ion beam are effectively trapped. The slits are usually maintained at a negative voltage of 20-40 volts with respect to ground to further insure trapping the electrons. Customarily, the Faraday cage will be connected to a commercial electrometer circuit that has a selection of input resistors, good stability and a current gain so that the output signal can drive a recorder.

Isotope ratio measurements have been improved by the simultaneous collection of two or more resolved ion beams. A dual collector can circumvent errors due to variations in ion beam production, conserve samples, detect ratio changes resulting from the preferential depletion of isobaric impurities, decrease the time of analysis and improve precision by cancellation of certain time dependent errors that are associated with the analysis.

The basic scheme for dual collection, as proposed by Nier, Inghram, et al (45,46) permitted one ion beam to proceed through a narrow defining slit to one collecting electrode and a second beam was intercepted on a plate. Both electrodes must have electron

suppressors in front of them to prevent secondary electrons from drifting out of the cages. A negative 20 volt bias is enough to repel most secondary electrons and not enough to interfere with the collection of the positive ion beam.

High quality d.c. preamplifiers and amplifiers should be used with the ion collectors. Vibrating reed amplifiers (47,48) measure currents as low as 10^{-15} amperes. They represent the ultimate electrometer for integral current measurements. The feature of the vibrating reed electrometer is the conversion of a d.c. input signal to an a.c. signal that can be amplified. The "vibrating reed" is a dynamic condenser in which the input current flows onto one plate of the capacitor. The other plate is vibrated at a fixed frequency and this periodic capacitance charge generates an a.c. signal. The resultant voltage is then amplified by a drift free a.c. amplifier. This device possesses long term stability and excellent response characteristics.

The output can be recorded on a strip chart recorder, in which the voltage output of the electrometer is plotted against time. In recent years, advances in digital equipment for use in the recording of signals from electrometers (49) have lead to greater precision and ease of obtaining results.

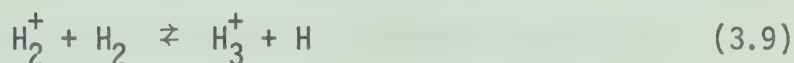
The simultaneous collection of ion beams was first suggested by Aston, and first implemented by Straus (50) in a study of nickel isotopes. Later workers (38,51,52) introduced modifications to improve upon this technique. The simultaneous collection systems of the past (51,52) used a center zeroed pen recorder so calibrated that deflections represented differences in the isotopic ratio of standards to

unknown samples. One of the most recent schemes developed by McCullough and Krouse (53) indicated higher precision. Rather than drawing lines through ratio lines and measuring distances between ratios, electronic digital equipment employing a printer, used its integrating property to do the time averaging.

3.6 Special Considerations For Hydrogen Isotope Analysis

A. H_3^+ Production

In hydrogen gas having a low deuterium content, the masses that are compared are two and three. The mass two is due to the H_2^+ ion with negligible contribution from D^+ ion. The mass three peak is composed of H_3^+ and HD^+ ions. For isotopic analysis it is only the contribution of HD^+ to mass three and not the entire number of mass three ions which is of interest. The H_3^+ ion formation presumably takes place through an ion collision with a neutral molecule.



The concentration of the H_3^+ ions was found by Urey and Teal (54) to be proportional to the square of the pressure. The contribution from HD^+ ions was proportional to the pressure. The total number of ions of mass three is given as

$$I_3 = ap + bp^2 \quad (3.10)$$

If I_3/p is plotted against the pressure, p and the straight line extrapolated to zero pressure, the intercept will give the true HD^+ contribution.

The intensity of the H_2^+ ions, I_2 , is very nearly proportional

to the pressure of the sample in the mass spectrometer at vacuum conditions. Therefore, plotting I_3/I_2 against I_2 will be sufficient to obtain the HD^+ contribution. In this manner then, the amount of H_3^+ can also be found since it is the slope of the straight line. This method was used by Kirshenbaum (9), Murthy and Rao (14), Friedman (11) and Horibe and Kobayakawa (12) to obtain a calibration for their standards. The ability of the source to reduce this contribution is a critical factor in design.

To eliminate secondary effects that occur in the instrument, such as static changes in the source or slight variations in the AC power from day to day, the comparison of an unknown to a standard is required. Thus the ratio, I_3/I_2 , for an unknown is compared to a calibrated standard ratio taken at the same time. The absolute value of an unknown usually cannot be found without a comparison to a standard, but Nief and Botter were able to calibrate their instrument to take into account the secondary effects so that an absolute measurement was obtainable.

B. Double Collection

Simultaneous dual collection of the mass intensities, I_2 and I_3 , using independent amplifiers reduces the problem of scanning over a wide voltage range that is required for a single collector instrument. It reduces the likelihood of different ion beam characteristics resulting from drastic changes in the high voltage. The precision is vastly improved, the samples are conserved and the time required for analysis is greatly reduced.

C. Sample Handling

The mass spectrometer requires that the sample to be analyzed

must be in the form of pure hydrogen gas. Therefore any samples that contain an isotope ratio that is to be analyzed must be converted to hydrogen gas, if the sample is not already in that form. This can be done effectively for simple hydrogen containing compounds such as H_2S , H_2O , CH_4 , etc by the use of a uranium furnace attached directly to the sample inlet of the mass spectrometer. This method of reducing hydrogen compounds eliminates the conditioning of the sample (10,11,12) and increases tremendously the quantity of samples that can be analyzed in a single period of time.

CHAPTER IV

DESIGN AND CONSTRUCTION OF A MASS SPECTROMETERFOR HYDROGEN-DEUTERIUM ANALYSIS4.1 Introduction

The analysis of isotopic ratios of hydrogen using mass spectrometry requires a high precision machine in order to obtain accurate and reproducible results. The primary design considerations include a method for simultaneous dual collection and a means to reduce the H_3^+ production. Two designs have been attempted. The first was similar to that described by Bigl (15), that is, a 180° mass analyzer with the source directly in the magnetic field. The machine did not give the performance expected for reasons that were obscure. It was abandoned in favour of a design with which there was more experience available at the University of Alberta. This mass spectrometer is referred to as a 90° sector analyzer with a Nier-type source. The machine is capable of handling both gas and liquid samples in that a uranium furnace has been placed directly into the gas inlet line.

4.2 One Hundred and Eighty Degree Magnetic Analyzer

The 180° analyzer has evolved from Dempster's work (29) and was improved by Bleakney (7) to the extent that hydrogen isotopes in enriched waters were capable of being detected. The latest improvements appeared significant enough, and provided encouragement, for us to adopt a design of a similar nature to that reported by Bigl (15). Bigl states that his instrument used simple grid optics rather than the conventional source with slot optics for the extraction,

acceleration and focusing of the ions. He reported little interference from H_3^+ . A diagram showing the interior of the instrument tried is presented in Figure 4.1-a. The external dimensions were 7.5 inches in diameter by 1.5 inches thick, and the body was constructed of type 316 stainless steel. A vacuum system consisting of three mercury diffusion pumps was used to provide an instrument operating pressure of less than 10^{-5} mm. of mercury.

A. Analyzer

The analyzer was made of two hollowed flanges sealed by using a circular aluminum gasket of 16 gauge thickness and ten 3/8" hexhead bolts threaded into the back flange. The source and collection systems were attached to the inside of the back flange. The flange is shown in Figure 4.1-a. The gas to be analyzed entered the instrument at E through a glass to Kovar seal. The gas pressure was monitored by a cold cathode gauge (55) commercially marketed by H. S. Martin and Company. The vacuum system was connected at port F through a glass to Kovar seal and the introduction of electronic leads was made through D. There were five Kovar leads used in the one seal and they were insulated from each other by glass. Two leads were used to transmit filament current, one each was used for the case and trap current feedback signals and one for the negative potential employed in the collector system.

Ions formed in the source, A, by the impact of electrons with hydrogen gas left through a grid. The source was in a magnetic field which had a strength of approximately 800 gauss. A permanent magnet made of bar magnets fabricated of Alnico and semicircular pole pieces was used. The pole pieces were six inches in diameter

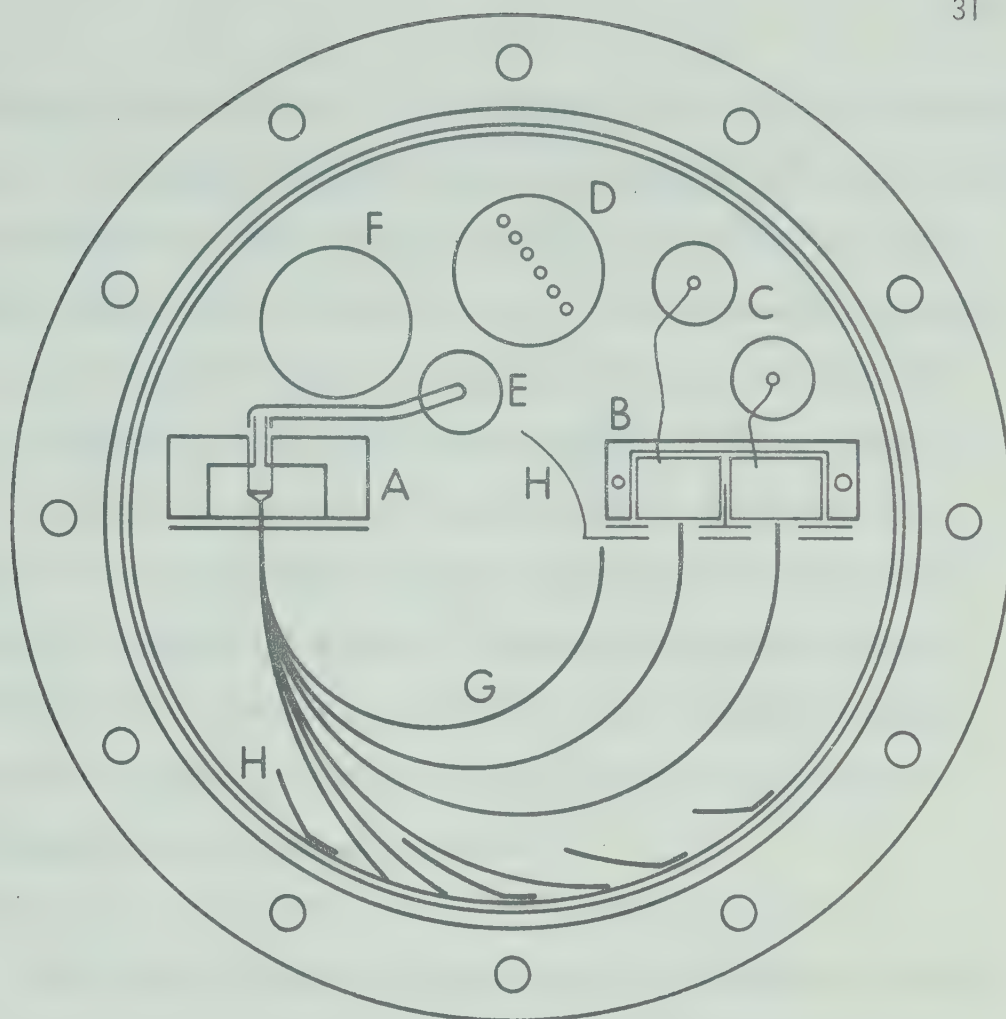


Figure 4.1-a INTERIOR VIEW OF 180° MASS ANALYZER

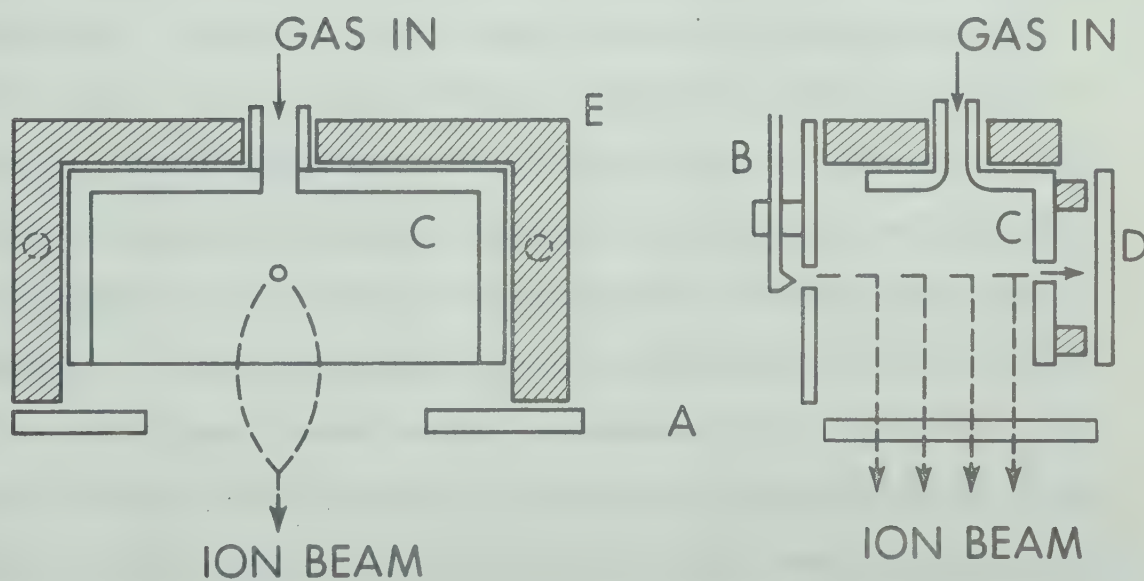


Figure 4.1-b CONSTRUCTION OF THE ION SOURCE

and permitted both the source and collectors to be within the magnetic boundary. As discussed by White (56), there should be fewer problems associated with ion production and collection if all parts of the instrument are within the magnetic field. This lessens the chances of stray or irregular fields, in particular those associated with magnetic boundaries, from influencing the path of the ion beam.

Ions leaving a source tend to separate because of the difference in mass and move along separate trajectories (eqn. 3.6) as depicted in Figure 4.1-a by G. To prevent extraneous noise in the collectors from particles other than those of masses two and three, several guards, H, were installed to block the passage of ions of heavier mass to the collectors.

B. Source

The source was of a simple nature and is shown in Figure 4.1-b. It was constructed of type 302 stainless steel and baked ceramic was used to provide the insulation necessary for the various sections. The case, C, was a metal box one inch long by one-half inch deep. There was an opening in the top to provide a passage for the gas, and openings in the front and back walls. These provided a path for electrons from the filament, B, to the insulated trap, D. The filament was a tungsten ribbon attached to posts of the same material. The filament had to be manually adjusted. That is, each time the filament burned out the replacement had to be centered over the opening in the case with the source still attached to the flange. The trap was a metal plate completely insulated from the case by the ceramic, E. The electrical isolation of the trap and case was required in order to provide a voltage difference between these

components for the collimation of the electron beam.

The collimating plate, A, had a grid through which the ions passed. The grid was made with wires welded across an opening in the plate. The opening was 0.25 inches by 0.10 inches and the width of this slit could be varied by welding thin metal pieces across the opening. A voltage was applied to this plate in order to accelerate the ions out of the source and into the magnetic field. The maximum voltage applied between the collimating plate and the case was 500 volts D.C. A Hewlett Packard model 712B was used as the regulated voltage supply. The regulated source was manually varied to provide the scanning function.

C. Collectors

Masses two and three were simultaneously collected in separate, shielded Faraday cages, B, depicted in Figure 4.1-a as electrons emitted by collision of the ions with the walls of these collectors were kept within the cups by the application of a negative potential of 45 volts. This voltage was applied to the guard plate, H, in front of the collectors. Several collectors which varied in size and shape were tried in an attempt to increase the sensitivity and resolution of the machine. Thin, tall rectangular cups, thin cones, and short square collectors were tried. Entrance slits, ranging from 10 mm to 2 mm in width, were used to improve the intensity of the ion beam.

The ion currents were transmitted along a stainless steel wire to C which was a Kovar-glass seal. This seal provided for insulation of the signals from the flange and at the same time permitted transmission from the vacuum to the external side of the flange, without

loss of vacuum. The signals were amplified by Cary 401 vibrating reed electrometers and then recorded on a Leeds and Northrup two pen strip chart recorder.

D. Operating Experience

Although the instrument was able to detect qualitatively the presence of hydrogen and deuterium, there was very little resolution of the peaks as seen in Figure 4.2. The gas sample was at a pressure of 1 cm of mercury in the inlet system and after passing through the leak provided an operating pressure of 10^{-5} mm of mercury in the source. The machine had a very high H_3^+ production rate and numerous changes in the design of the source and collector system failed to improve on the formation of H_3^+ and the resolution desired.

Changing the slit width on the collimating plate changed the peak shapes slightly, but provided little or no change in the actual peak height, that is, the intensity of the ion beam collected. Reducing the width of the slit should have produced a more compact beam leading to a sharper, more resolved peak. Adjustment of the voltage difference between the case and trap increased the trap current, providing only minute changes in the peak intensities, indicating that the efficiency of the electron beam was at a maximum. Scars on the side of the case indicated that most of the electron beam was directed to the sides of the case. This, in turn, showed that the filament was unsatisfactorily centered over the opening in the case. Electrons that did not reach the trap could not provide proper ionization of the gas and this was probably the reason for significant H_3^+ production.

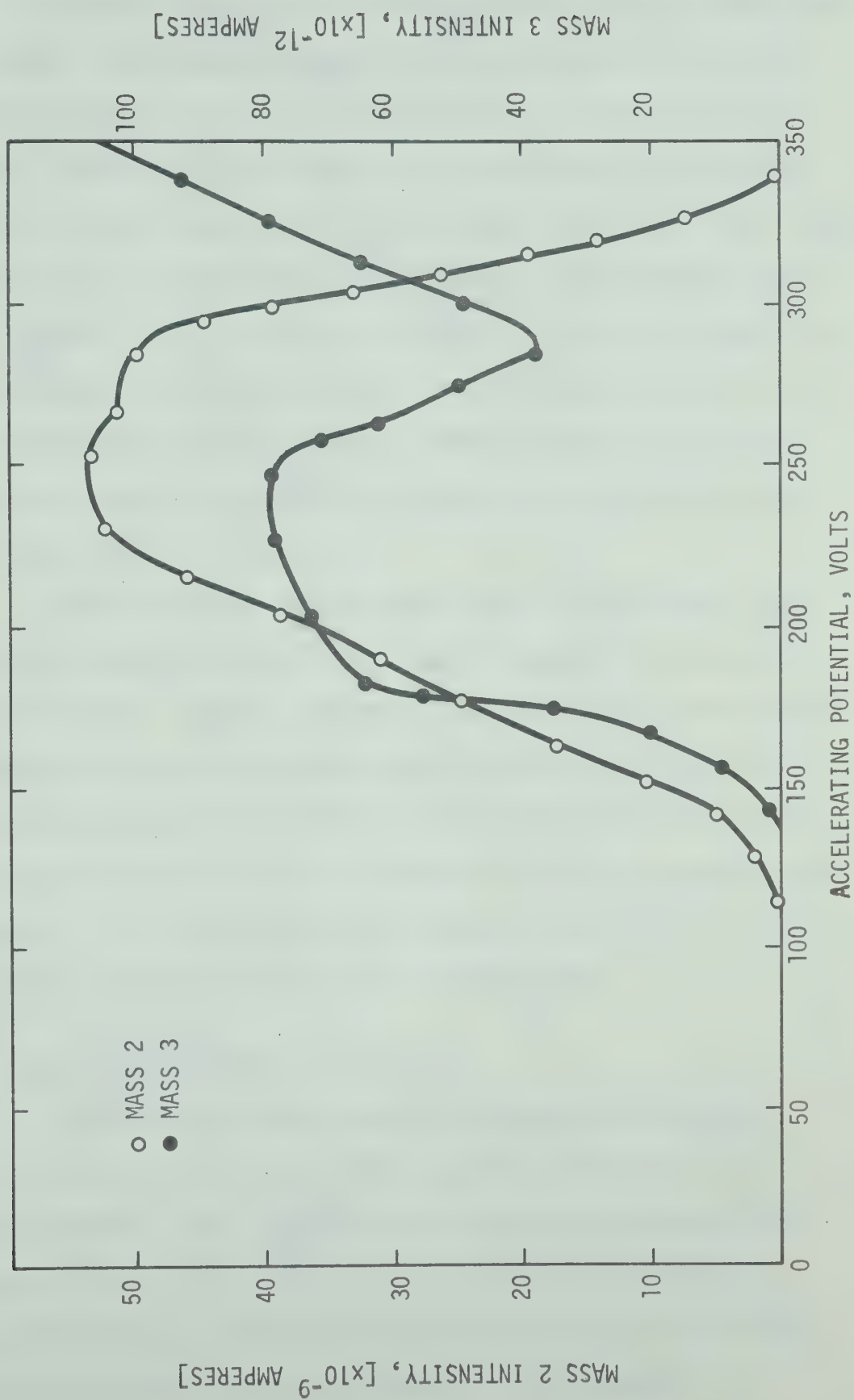


Figure 4.2 SHAPES FROM 180° ANALYZER

The peaks that were obtained by scanning the gas sample were ill-defined. This normally results from the entrance slits to the collectors being too wide or the energy of the ion beam being non-uniform. With narrow slit widths, the ion beam should have entered the collectors very abruptly, giving the peak a very sharp side. Then, if the ion beam is smaller than the collector width, the peak should have a flat top. This, as noted in Figure 4.2, was not the case, the peaks suffered from "tailing effects", the tops were not flat and the signal varied from sample to sample. Different types of collectors were tried as well as adjusting the entrance widths but the results were always similar to Figure 4.2.

The difficulties may have been due to the fact that type 302 stainless steel, which is a non-magnetic material was used to build the source. However, when individual parts were held close to the permanent magnet, these pieces were attracted to it. This led to speculation that fields set up by these parts could have been of sufficient strength to distort the ion beam during its generation and collimation. This would give a large energy spread to the ion beam and certainly would result in poorly resolved peaks.

4.3 Ninety Degree Magnetic Analyzer

The second mass spectrometer constructed for observing masses two and three with simultaneous double collection is a 90° sector instrument. This is basically a Nier-type spectrometer and a schematic of the interior of the 2.5 inch radius instrument is given in Figure 4.3. The body and all metal parts were constructed of 316 stainless steel since this material is non-magnetic. A

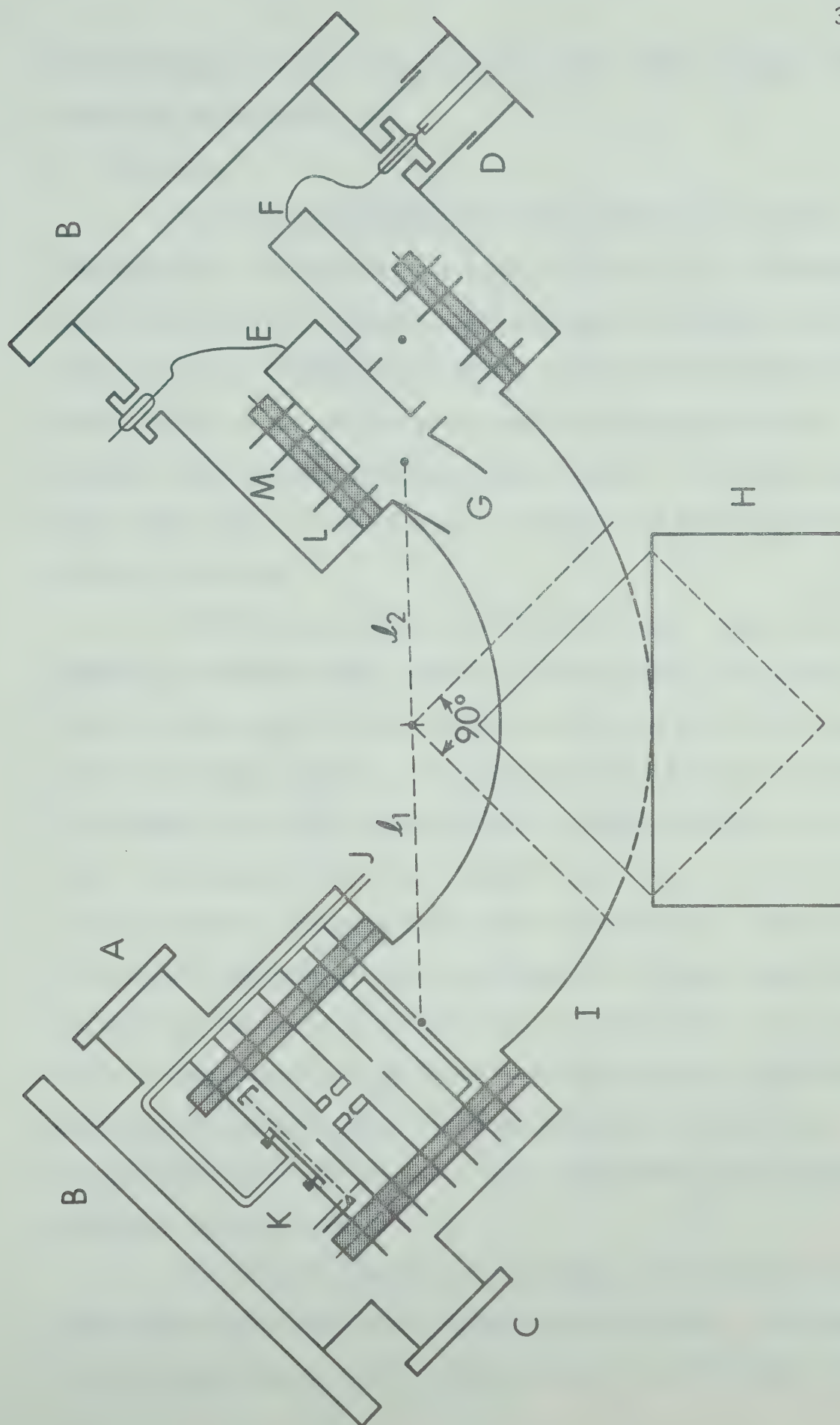


Figure 4.3 NIER-TYPE 90° SECTOR INSTRUMENT

uranium furnace has been incorporated so that simple hydrogen compounds can be analyzed.

A. Ion Source

The ion source designed for this instrument is shown schematically in cross-sectional views in Figure 4.4. The source consists of a series of plates, each with basic dimensions of 1.750 inches square by 0.03125 inches thick. They are held together by means of four studs, one at each corner of the plates, and are separated and insulated by baked ceramic spacers. The spacers are each 0.250 inches by 0.375 inches in diameter and are designed to slip over the studs.

The first two plates constitute the case. They are grounded together by stainless steel spacers in place of the lava spacers. There is a box welded to the underside of the top plate that serves as the ionization chamber. The filament support is also attached to the upper plate and is held in place by Allen head bolts threaded 3-56. The chamber contains an electron trap, i.e., an insulated cup that collects electrons coming from the filament. There are two slits within the chamber, one just beyond the filament support and the other at the entrance to the trap, 1.0 inches away. These slits are 0.10 inches high by 0.25 inches wide and provide a collimating action on the electron beam. Whatever electrons fail to make it through these slits hit the case, i.e., the chamber walls, and give the resulting case current.

The filament consists of a tungsten ribbon mounted between two tungsten leads which are insulated by pyrex glass. The ribbon is 0.25 inches long by 0.025 inches wide and is 0.003 inches thick.

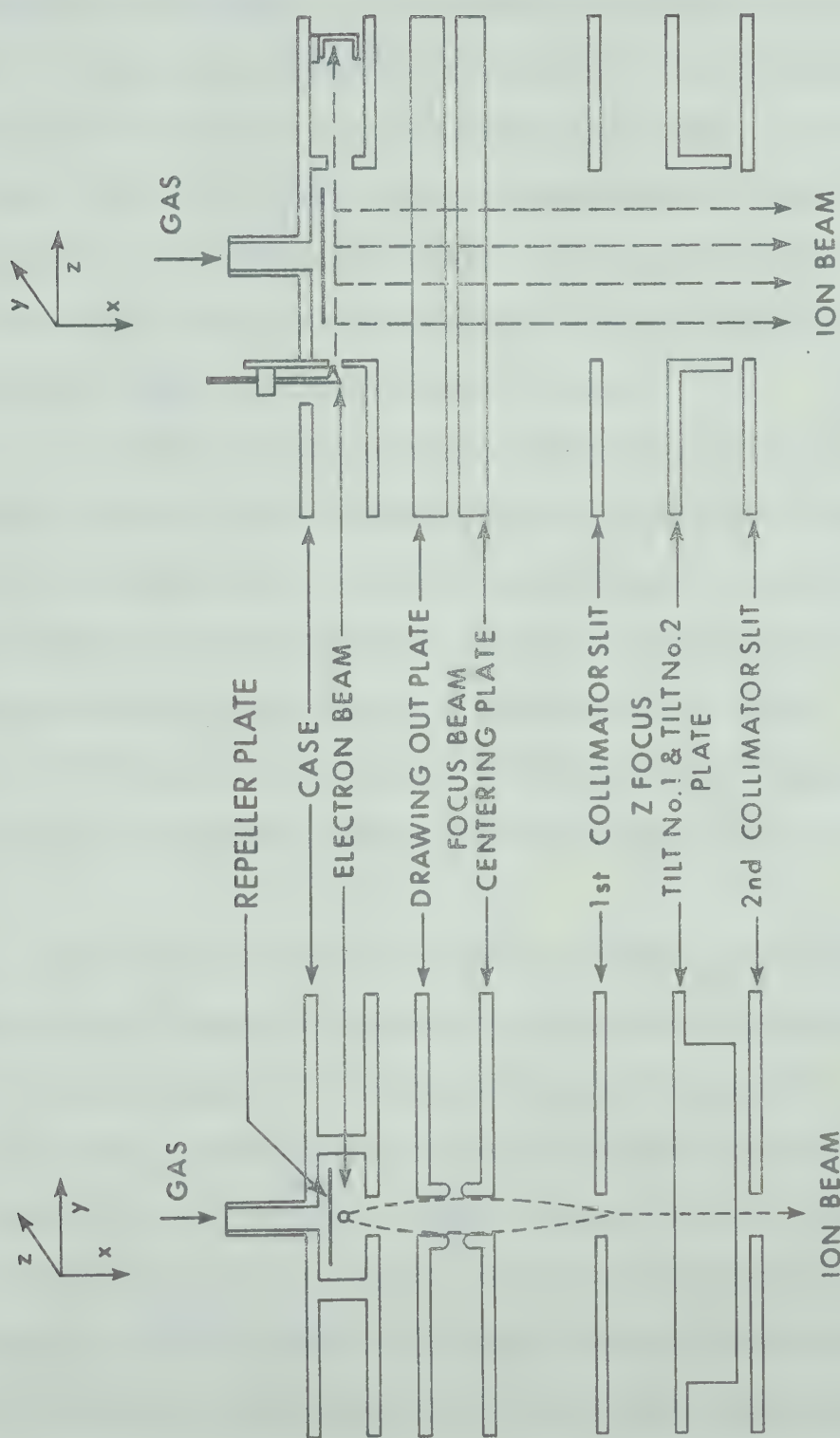


Figure 4.4 SCHEMATIC DRAWING OF ELECTRON BOMBARDMENT SOURCE

The filament current of four to five amperes is supplied by a regulated supply based on a design by Russel and Koller (56). The electrons are accelerated by a difference of potential of 160 volts between the case and one side of the filament. The electrons pass through the slits and are measured on the trap plate. There is an additional slit that is part of the filament support that is 0.20 inches wide by 0.05 inches in height. The filament holder ribbon is lined up with slits outside the source, so as to insure that the filament will eject electrons towards the trap.

The total electron emission, consisting of trap and case currents, is about 3.0 milliamperes and up to one-third is attributable to the trap current. There is a difference in potential of 40 volts between the trap and case to prevent the escape of electrons from the trap and to help pull more electrons to the trap. The source of these potentials, as well as the regulated filament current, is the emission regulator, whose circuit diagram is shown in Figure 4.5

The emission regulator supplies a stable, ripple-free current to the filament and in addition provides for different potential settings between the filament and case and between the case and trap. The trap current signal is sent to the emission regulator which has a feed back circuit to keep the trap current constant. Any variation in the trap current will lead to differences in the ionization of the gas sample. This means that the characteristics of the ion beam are altered and this in turn will cause changes to occur in the intensities of the ion current for masses two and three. The feed back circuit permits the filament current to adjust to keep

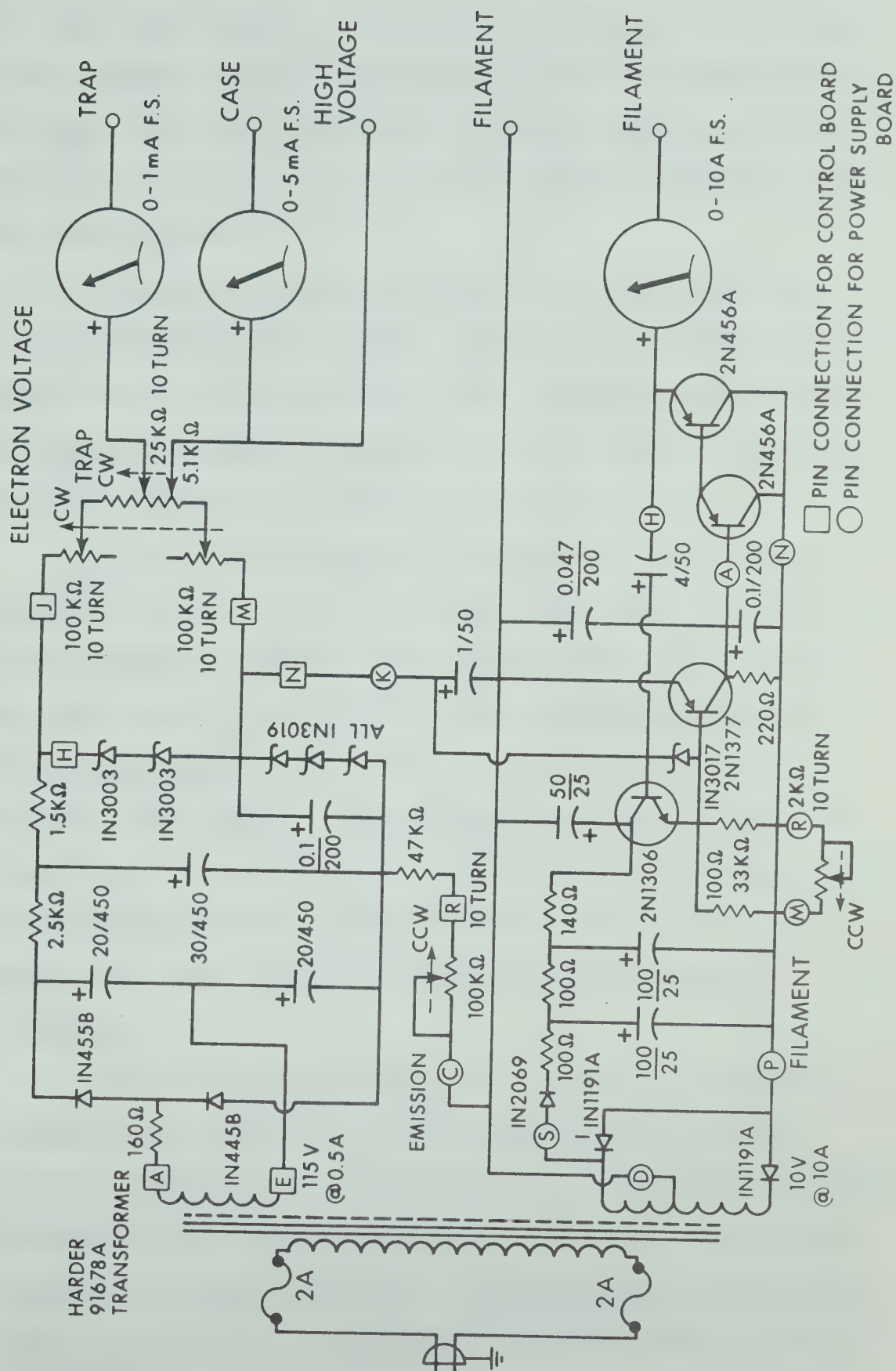


Figure 4.5 EMISSION REGULATOR CIRCUIT DIAGRAM

the trap current constant. The ionization efficiency of the source can be changed by varying the potential difference between the trap and case. This potential difference should be adjusted to maximize the trap current thus making the greatest number of electrons available for ionization.

Magnets, external to the source, are used to keep the electron beam compact and uniform. These focusing magnets are permanent Alinco bar magnets having a field strength of 100-200 gauss. The magnets are placed in a yoke and are positioned so as to give a maximum trap current for a particular emission current.

The gas is introduced to the source via a 0.125 inch diameter tube that is welded to the upper case plate. It then passes through the electron beam to become ionized and these ions are drawn downward by an electric field between the case and the drawing out electrode. In order to reduce the residence time of the ions in the source, a repeller plate was installed as shown in Figure 4.4. The repeller is 0.25 inches long by 0.125 inches wide and is held between 20 and 50 volts negative with respect to the case voltage. This voltage difference results in lowered H_3^+ production.

The accelerating potential for the ions is produced by a high voltage source applied to the entire series of plates, through a voltage divider. Figure 4.6 is a schematic of the voltage divider which is similar to that used by Dietz (57). As its name implies, the voltage divider splits the high potential using resistances of various sizes. Each plate in the source then receives a proportional amount of the total voltage that is supplied to the

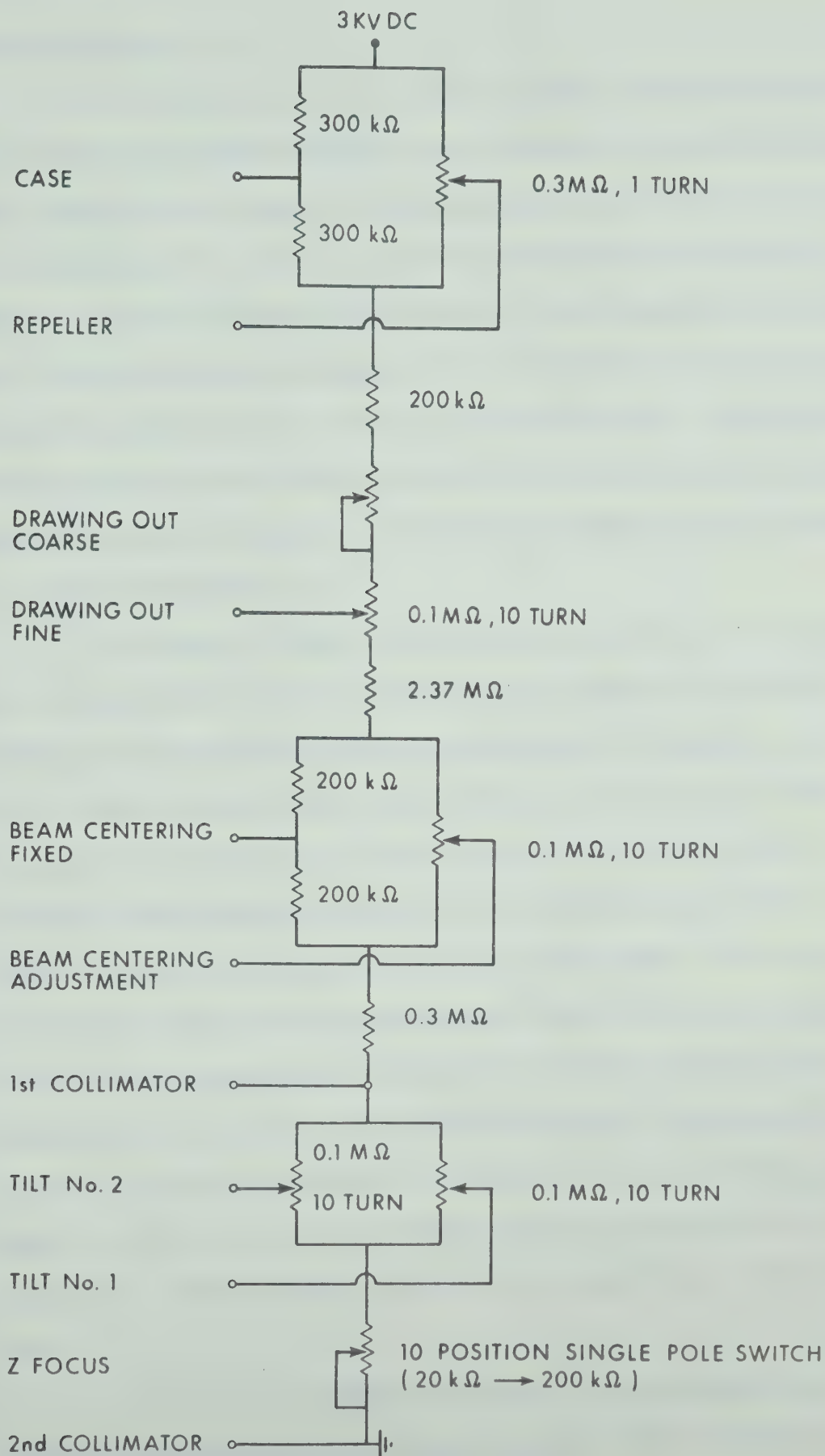


Figure 4.6 CIRCUIT DIAGRAM FOR VOLTAGE DIVIDER

voltage divider.

The functions of the series of plates comprising the source are generally to shape and focus the ion beam as it leaves the case. Thus, these plates behave in much the same way as prisms and lenses do in light optics. Although work has been extensively done on electron optics (58), few descriptions of the characterization of slit lenses (59,60) or the application of electron optical techniques to the ion optics of slit lenses are available (61). A description of the various source plates and their functions will explain what happens to the ion beam as it is formed and shaped prior to ejection into the analyzer tube.

As shown in Figure 4.4 the ions leave the case through a 0.4 inch by 0.08 inch slit. The Nier-thick lenses (62) are the drawing out plate and the focusing half plates. The plates are 0.025 inches thick and have an edge which is 0.090 inches thick. The drawing out plate has a 1.000 inch by 0.15 inch slit which partially compensates for spherical and chromatic aberrations as the ions are drawn from the case. The focus half plates provide both focusing and beam centering action, and the voltage of each plate is independently adjustable. The beam is focused so that its focal length terminates at the first collimating plate. The potential gradient in the region between the focus half plates and the collimator is small so that beam divergence from field penetration is negligible. The collimator slit is 0.40 inches long by 0.060 inches wide.

The maximum transmission through the source and analyzer is obtained by strong focusing in the y-direction (see Figure 4.4) and

is accomplished by adjusting the potentials of the Nier thick lenses. Focusing in the z-direction must be done so that the focal point occurs beyond the first magnetic boundary of the analyzer. Since the focal length is so long, only weak lens action is required in the z-direction. To overcome the deficiency of having non-uniform intensity of emission, electrical focusing is done by using an independent slit lens placed at right angles to the main lenses. This z-focus lens is composed of two plates separated by a distance of 0.65 inches. Each plate has an edge of 0.20 inches in height. Independent adjustment of voltage on the half plates provides centering action for ion beams travelling through the analyzer.

The two collimating plates provide the significant focusing in the y-direction. The second collimating plate has a 0.4 inch by 0.04 inch slit. The remaining potential from the voltage divider is applied to this plate. The values of the resistances required for the voltage divider are shown in Figure 4.6 and were found by trial and error. The selection of resistances used permits considerable flexibility in adjusting the peak shapes.

The connections from the source plates to the voltage divider were made through stainless steel leads sealed in ceramic. The leads from the source to these connections were stainless steel wire welded individually to each plate. These wires were insulated from each other in the source chamber by pyrex glass tubing.

B. Magnetic Analyzer

As stated in Section 3.4, Barber (41) and others (40,42) have shown that if a slightly divergent beam of ions, all at the same momentum, passes through a homogeneous magnetic field between two

V-shaped poles, and if the particles enter the field perpendicular to the boundaries and are bent through such an angle that the ions leave the field perpendicular to the boundary, a refocusing of the ions takes place. The nature of the focusing is such that the source of the ions, the apex of the wedge shaped magnetic field and the point of refocusing all lie on a straight line. This focusing arrangement has been used by Nier (37), Kirshenbaum (63) and in a double focusing mass spectrometer (64) and is employed in the present design.

As shown in Figure 4.3, the ion source, K, is enclosed by a metal barrel TIG (tungsten inert gas) welded to a length of tubing which is the analyzer. This tube is 0.65 inches thick, 2.00 inches deep and has a mean radius of curvature of 2.50 inches. The ion collectors which are housed in a cylinder similar in construction to the source barrel are at the other end of the tube. These cylinders were made from 3.50 inch outside diameter pipe which has a wall thickness of 0.25 inches. Flanges, B, having an outside diameter of 5.750 inches and thickness of 0.50 inches are welded to one end of each of the cylinders. The flanges are grooved to accept an aluminum gasket. A cover flange is attached with eight 7/16 inch bolts placed symmetrically around the flange and the assembly is sealed by applying a torque of 150 inch-pounds to the bolts. The length of the cylinders are 3.50 inches. The pump lead, C, and electronic lead, A, were made from 1.50 inch outside diameter tubing having a 2.00 inch diameter flange welded to the open end.

A permanent magnet is used for the analyzer. The magnet

is comprised of a metal yoke of the type used in a commercial MS-10 mass spectrometer manufactured by Picker-Nuclear and 10 magnetized ceramic slabs 3.50 inches square by 0.50 inches thick. Rather than constructing pole pieces, these slabs were turned on a corner so that the edges were 45° from the horizontal, thus giving the wedge shape required for 90° sector instruments. The ceramic slabs were manufactured by Permag Central Corporation. The air gap between the faces of the magnet is 0.750 inches and results in the magnet having a field strength of 1850 gauss. The magnet is set on a brass platform and leveling screws permit adjustment of the position of the magnet relative to the analyzer tube. There is sufficient room for sideways adjustment. One must consider that the magnetic boundaries are not the physical boundaries of the magnet, but will be found about one air gap from the edge as depicted in Figure 4.3 as a dotted line around the magnet.

C. Vacuum System

The operation of the mass spectrometer requires a high vacuum environment in order to eliminate the adverse effects of residual gases, for example, ion scattering and background. The vacuum required is in the order of 10^{-6} to 10^{-8} mm of mercury. By keeping the pressure of the sample in the source low, the H_3^+ production is kept to a minimum. This phenomenon was discussed in Section 3.6. The vacuum requirements for this mass spectrometer are met by using an ion pump and two mercury diffusion pumps.

The ion pump is attached to the source head of the mass spectrometer and is employed to keep the metal section of the system under high vacuum. An all-metal flanged valve made by Varian Associates connects the ion pump to the flanged port on the mass

spectrometer. The flanges are 2.0 inches in diameter and the valve ports are 1.5 inches. Soft copper gaskets from Varian Associates are used in the flanges and these, when compressed, provide an excellent seal. The vacuum is monitored by a cold cathode type vacuum gauge which is built into the ion pump assembly.

The ion pump is a Varian Model 921-0013 and has a 15 litre per second pumping speed. As its name implies, the ion pump is a vacuum pump that emits electrons to ionize neutral gas molecules. The electrons are produced when a high voltage is applied between a titanium cathode and a hollow metal anode in a magnetic field. The positively charged ions travel toward the cathode and become buried as they strike it. At the same time, the bombarding ions free titanium from the cathode which deposits on the pump walls where it attracts chemically active gases such as oxygen, hydrogen, or nitrogen. It is capable of vacuums to 10^{-8} mm of mercury.

The mercury diffusion pumps are used to keep the sample inlet systems evacuated. The two pumps, P-1, a high capacity three stage diffusion pump and, P-2, a two stage pump are constructed of glass and operate in the following manner. Mercury is evaporated from a heated sink, and vapours stream out of jets in a downward direction (each jet is a stage) with supersonic velocities. This vapour hits the water cooled walls of the pump, condenses, and flows back into the sink. A transfer of momentum from the mercury vapours to gas molecules drives the gas towards a fore pump. These pumps are capable of 10^{-7} to 10^{-8} mm of mercury. A liquid nitrogen trap is necessary upstream of the diffusion pump to prevent mercury from entering the mass spectrometer and forming amalgams which will cause

a drop in vacuum because of their vapour pressure.

The forepumps are rotary vane type capable of 10^{-3} mm of mercury. The models used are Duo-Seal and Cerro Hyvac 4. With the assembly of ion pump and mercury diffusion pumps there has been no problem in maintaining a system vacuum of 10^{-7} mm of mercury.

Normal sample pressures decreases the instrument vacuum to 10^{-6} to 5×10^{-6} mm of mercury. All metal to glass seals are made of kovar and pyrex unions. The kovar has a coefficient of expansion similar to that of pyrex. Metal to metal seals employ flanges with soft, compressible gaskets made of copper or aluminum, with the flange bolts set to a tension of 140-150 inch pounds.

D. Collection System

The instrument was built to specifically analyze masses two and three. As a result, the collectors have been built to simultaneously obtain the ion beams produced by these masses. The placement of the collectors is shown in Figure 4.3. They are two box-shaped Faraday cups and have a depth of 1.25 inches in order to eliminate the release of secondary electrons caused by the ions striking the collector walls.

The mass two collector, E, has slit dimensions of 0.50 inches by 0.40 inches. This enables the ion beam from hydrogen to project a very wide peak, with an essentially flat top. The mass three collector, F, has a narrower slit of 0.40 inches by 0.30 inches to provide some discrimination to the signal. The procedure used to calculate the position of these cups so that dispersion effects from each beam will have negligible effects on the signal to the other collector is described in Appendix A. The distance between

the cups is 1.25 inches.

Guards and repeller voltages are used to reduce secondary electron emission, by preventing electrons formed by collisions of ions with walls of the collectors and analyzer tube from entering the collectors. The guards are rectangular metal pieces welded to the primary slits and are designated G. The guard placed on the top edge of the mass two collector is designed to prevent reflected electrons and ions from a stream of mass one ions from entering the collector. The guard above the mass three collector prevents stray ions from mass two and subsequently formed electrons from entering F. Electron suppression plates L and M are used to prevent the electrons formed within the collectors from leaving. These plates are subjected to a negative potential of 45 to 67 volts D.C.

The repellers, i.e., electron suppression plates, and collectors are electrically isolated from each other by the use of ceramic sleeves of the same dimensions as those used in the source. The collector assembly is attached to the analyzer using 4-40 threaded rods. These rods go through the corners of the various plates which have a dimension of 1.75 inches by 1.75 inches. The repeller plates also serve as primary defining slits for the resolved ion beams. The slit for mass two is 0.60 inches by 0.50 inches and the slit for mass three is 0.40 inches by 0.30 inches.

E. Detector System

The signal from the mass two beam is of the order of 10^{-10} amperes and is transmitted to a preamplifier along a thin stainless steel wire welded to the collector and connected to a kovar in glass sealed rod. The seal is held in place by compression

of a viton O-ring with a 9/16 inch nut. This type of connection is also used to transmit the negative potential to the repeller plates. Non-magnetic brass sleeves, D, shield the external connection from the collectors to the preamplifier. These serve to prevent noise from external sources such as the fluorescent lights, adjacent rheostats and stray magnetic fields from interfering with the minute signals from the collectors. The sleeves telescope to provide easy attachment and are held in place by set screws to keep the connection secure from vibrations.

The signal from each collector reaches the Cary model 401 vibrating reed electrometers through preamplifiers. A schematic of the actual electrical plan is shown in Figure 4.7. The signals from the collectors are preamplified and changed to voltages in the electrometers. Then, an integrating digital volt meter (Dymac model DY 2401A) integrates the input voltage from each electrometer over a selected time and changes it to a proportional frequency through a voltage to frequency converter (Dymac model DY 2211B). In passing through the counter section, this frequency is compared to a standard time base frequency which, in this case, is the frequency of the monitored peak voltage of mass two. The ratio of the voltages of the two peaks is then displayed on a Hewlett Packard 562A digital printer. A function switch, details of which can be found elsewhere (53), is used to obtain the ratio of one beam to another, the inverse of this ratio, the output of each electrometer or null balances of the digital voltmeter and converter.

The peak shapes may be traced on a two channel Bristol model pen recorder. This is useful when tuning the instrument, or

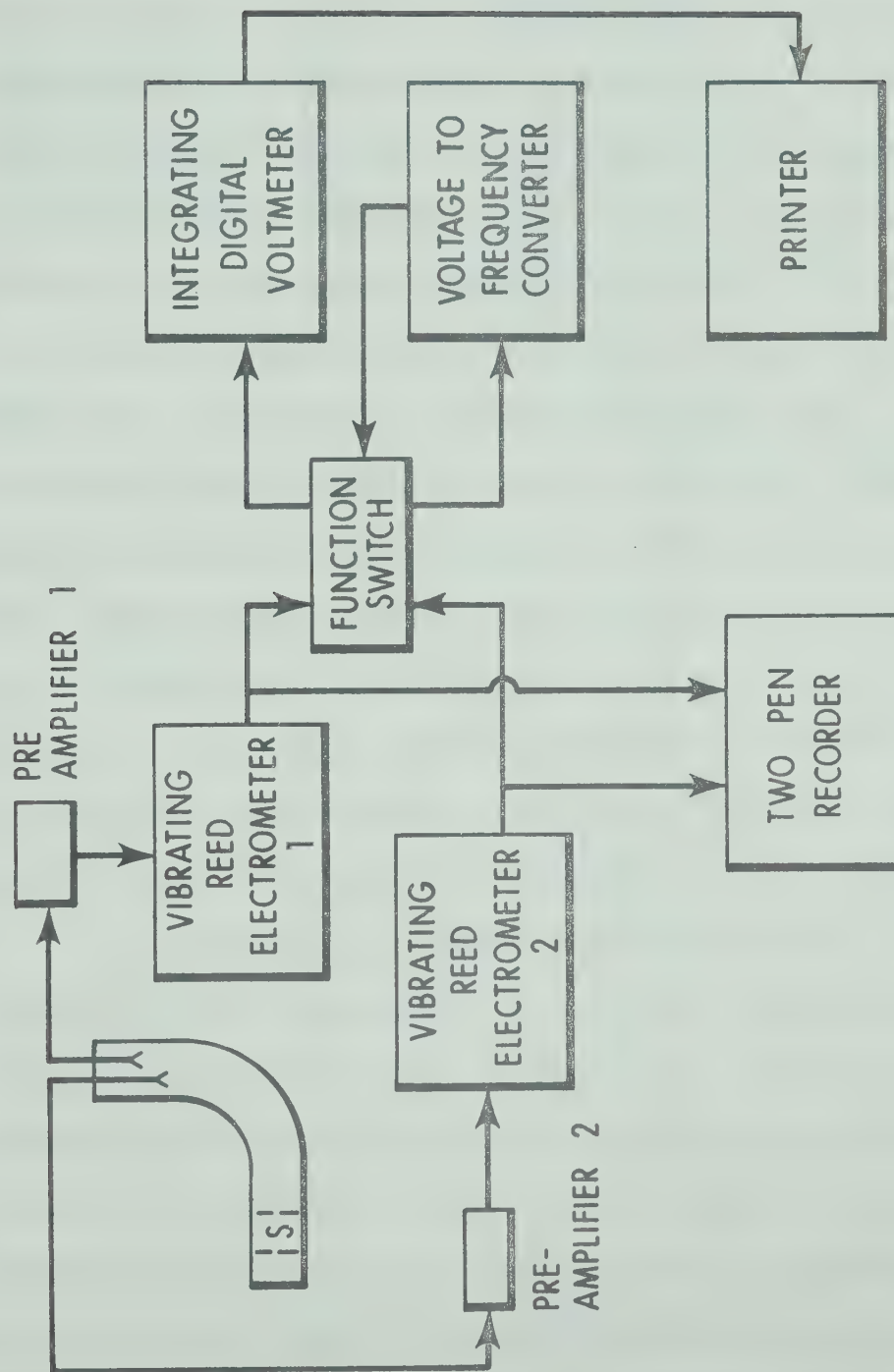


Figure 4.7 SCHEMATIC DIAGRAM OF MEASURING SYSTEM

occasionally checking their locations. The peaks are scanned by progressively increasing or decreasing the accelerating voltage over a selected time interval. Figure 4.8-a shows the electrical connections used for scanning to a maximum of 2500 volts. The type of scanning function is chosen using a Hewlett Packard model 3300A function generator which has a variable amplitude to give different voltage range scans. The high voltage supply, a Kepco model ABC 2500, has a built-in voltage programming function. The frequency of the function used can be set from .001/second to rates as high as 10K/second. This frequency sets the time for the scan. A Hewlett Packard model 3440A digital voltmeter coupled with a voltage divider is used to locate the voltage at which the scanned peaks occur. The voltage divider is required since the high potential used is greater than the voltmeter can receive. In this manner, the location of the peaks can be ascertained to within one volt. The mass associated with the peak voltage can be identified using eqn. 3.6 since radius and magnetic field strength are fixed.

Unfortunately, the Kepco high voltage supply is not adequate to span the entire mass range. The normal mass spectrum requires the voltage to scan from 300 volts to 3200 volts. A North Eastern Scientific Corporation model RE 5001 regulated high voltage supply is placed in the circuit as shown in Figure 4.8-b. The voltage available from this supply is 5000 volts making a realizable source of 7500 volts for scanning. Since the Kepco configuration is required to do the scanning, the maximum range available is 2500 volts, i.e., if the voltage of the RE 5001 is set at 1000 volts, the scanning range will be 1000 to 3500 volts.

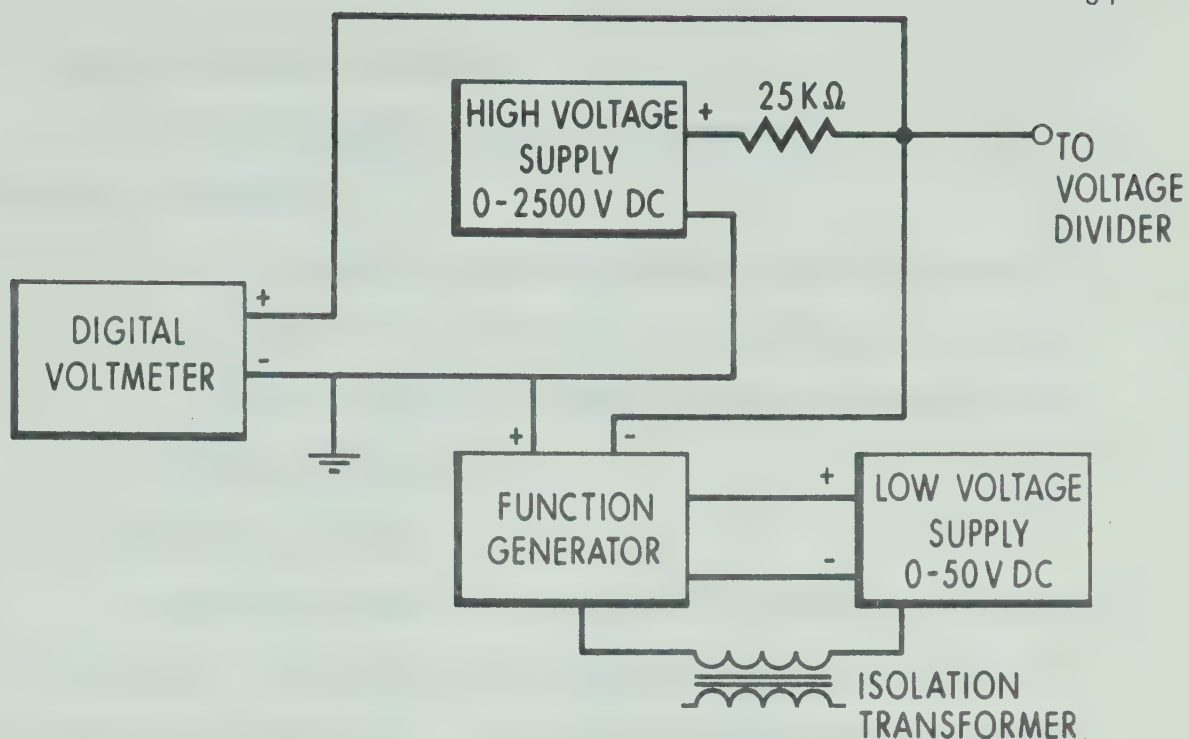


Figure 4.8-a SCHEME FOR VOLTAGE SCANNING TO 2500 VDC

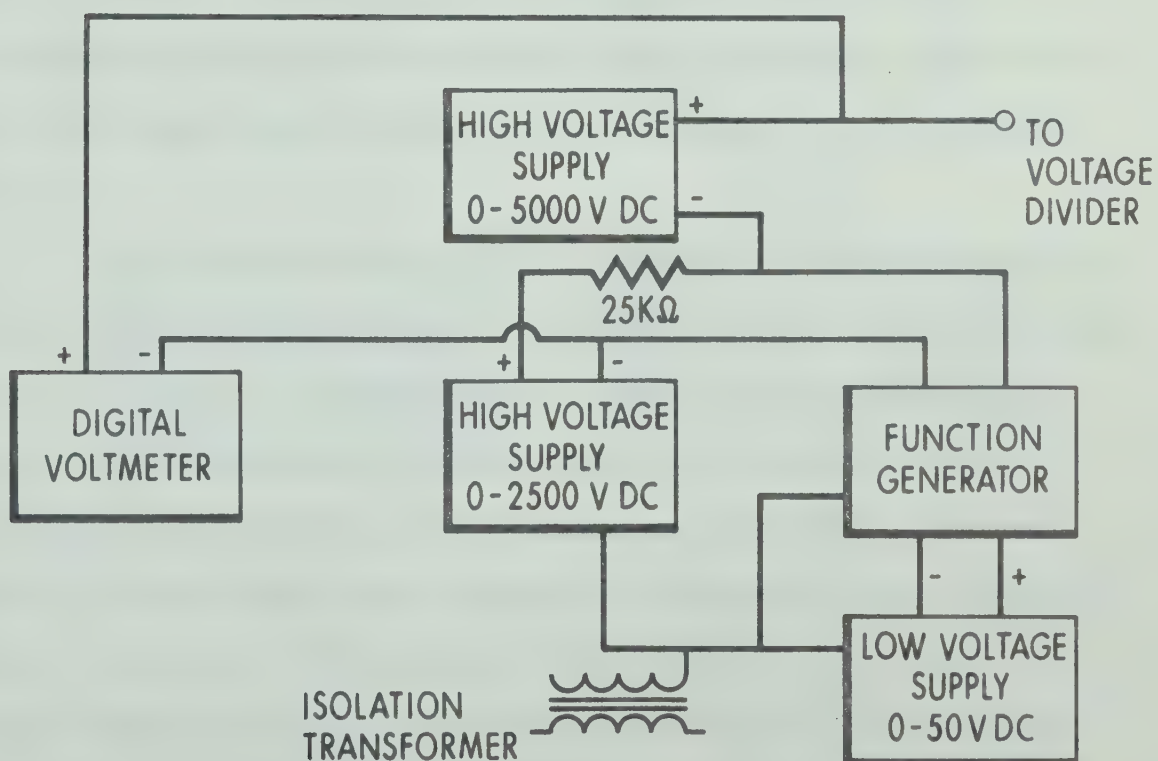


Figure 4.8-b SCHEME FOR VOLTAGE SCANNING TO 7500 VDC

F. Sample Introduction Systems

Two sample systems have been incorporated in the design of the mass spectrometer

- i) a system for samples containing only hydrogen gas
- ii) a system which utilizes a uranium furnace to allow for the analysis of simple hydrogen compounds such as H_2O , NH_3 and H_2S .

i) Hydrogen gas samples

Figure 4.9-a shows the gas sample introduction system used. It is based on a rapid valve system devised by McKinney et al (51) and Wanless and Thode (52). Two complete systems with gas volumes, mercury leveling reservoirs and capillary leaks are attached to the mass spectrometer through a system of magnetic solenoid valves. In operation these valves deliver one sample to the mass spectrometer while the sample from the other system is flushed in a waste vacuum line.

The sample bomb, A, of 20 cc capacity is inserted into the system using a 10/35 $\frac{1}{8}$ glass joint. The air trapped between the stop-cocks, V-1 and V-2, is pumped away by opening the three-way glass valve V-3 to the mercury diffusion pump, P-1. The gas is then deposited in the reservoir, C, which has an adjustable volume and hence a pressure that can be increased or decreased by adjusting the height of mercury in the column. A check valve, V-4, prevents mercury from rising too high and entering the leak. The pressures, or more specifically the intensities of the mass two peak, must be matched between samples to facilitate the comparison of the samples for their deuterium content. The gas sample then flows through a

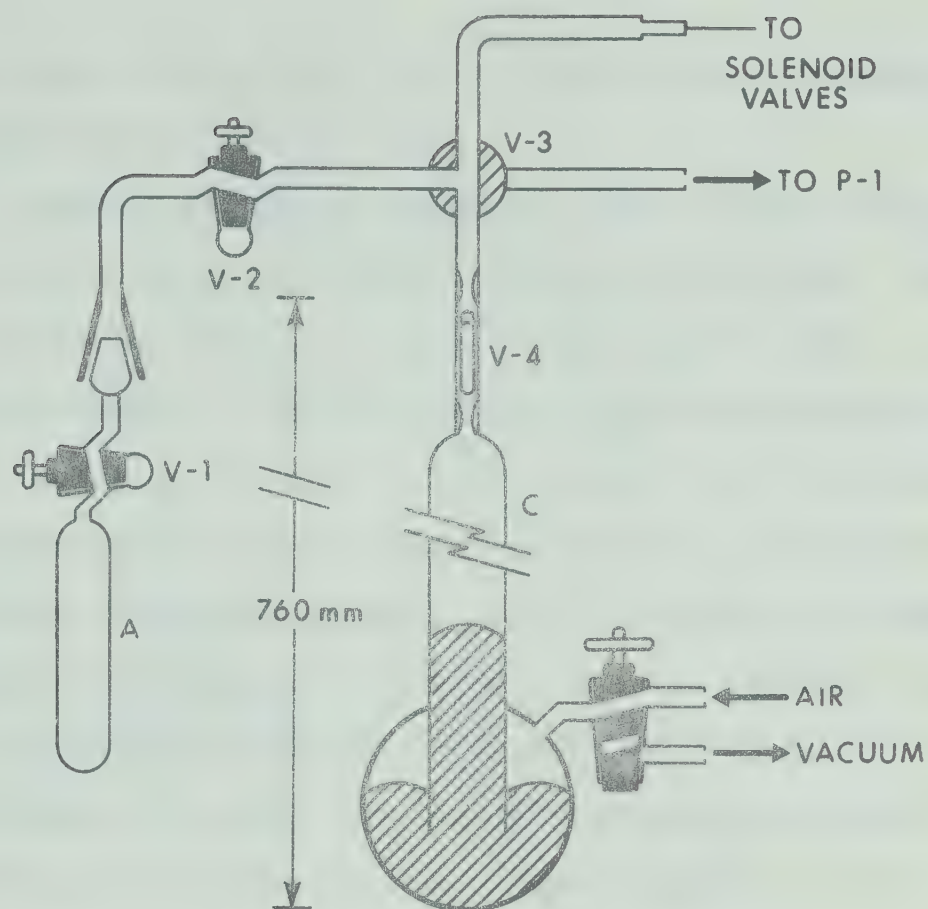


Figure 4.9-a GAS SAMPLE INTRODUCTION SYSTEM

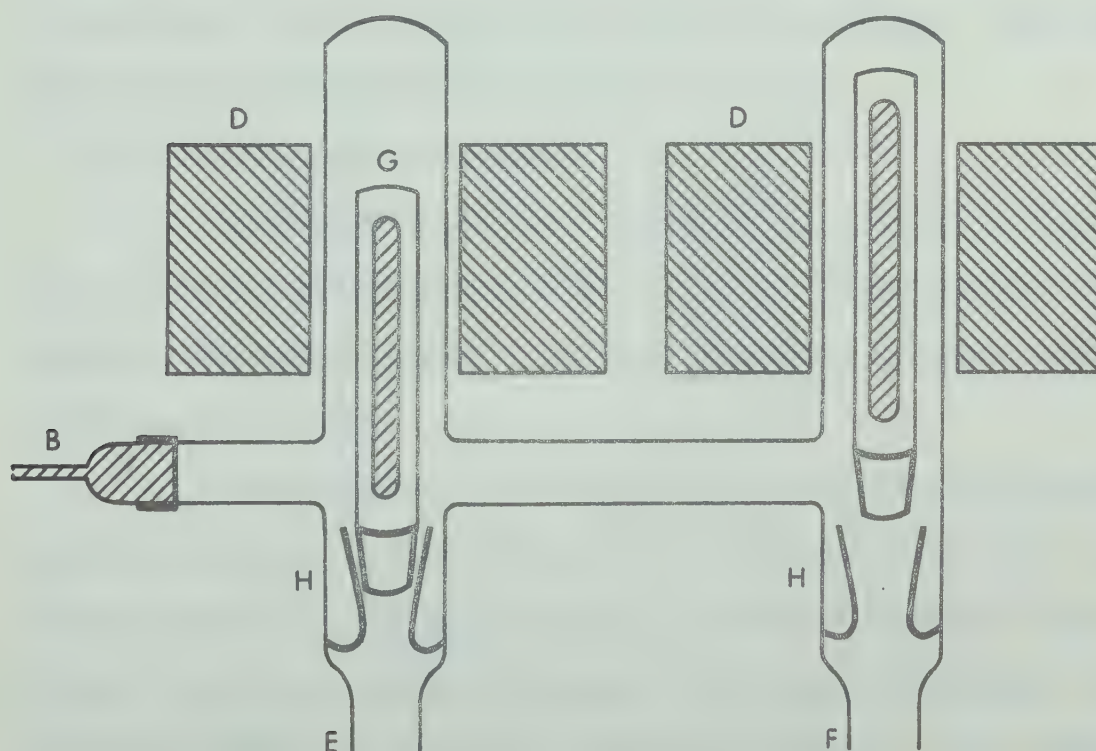


Figure 4.9-b RAPID SOLENOID VALVE SYSTEM

stainless steel capillary leak, B, which has an internal diameter of 0.0008 inches and is 14 inches long.

From the leak the gas reaches the glass solenoid valves. There are two valves per gas system as shown in Figure 4.9-b. The plugs, G, are metal enclosed in glass and the plugs fit into a 10/20 $\frac{3}{4}$ glass joint, H. The first valve is closed when admitting a gas sample as the port E leads to a waste vacuum line. The gas then flows through the line from the leak B and into the second solenoid, normally open, and through the port, F, into the source of the mass spectrometer. To introduce a sample from the second system to the source, an identical process takes place with the other set of solenoid valves. The valves used for the first sample have their actions reversed, i.e., the first valve opens to permit gas to be removed by the waste vacuum line and the second valve closes to prevent gas from the other system from entering through F and being swept away by the vacuum applied to the port, E.

ii) Simple hydrogen compounds

The second sample inlet system which is shown in Figure 4.10, uses a uranium furnace held at 600°C to reduce hydrogen compounds. The furnace makes it possible to analyze hydrogen compounds rapidly and reliably.

Liquid samples, for example H_2O , are introduced through a silastic stopper, B, made of Dow Corning fluorosilicone with a hypodermic needle, D. The needle is 10 μL in size and samples ranging from 1 μL to 10 μL can be introduced. The sample is placed in the expansion volume, A, which has a capacity of 1000 cc. This vessel is heated to 100°C by heating tape, H-2. The vapourized sample then

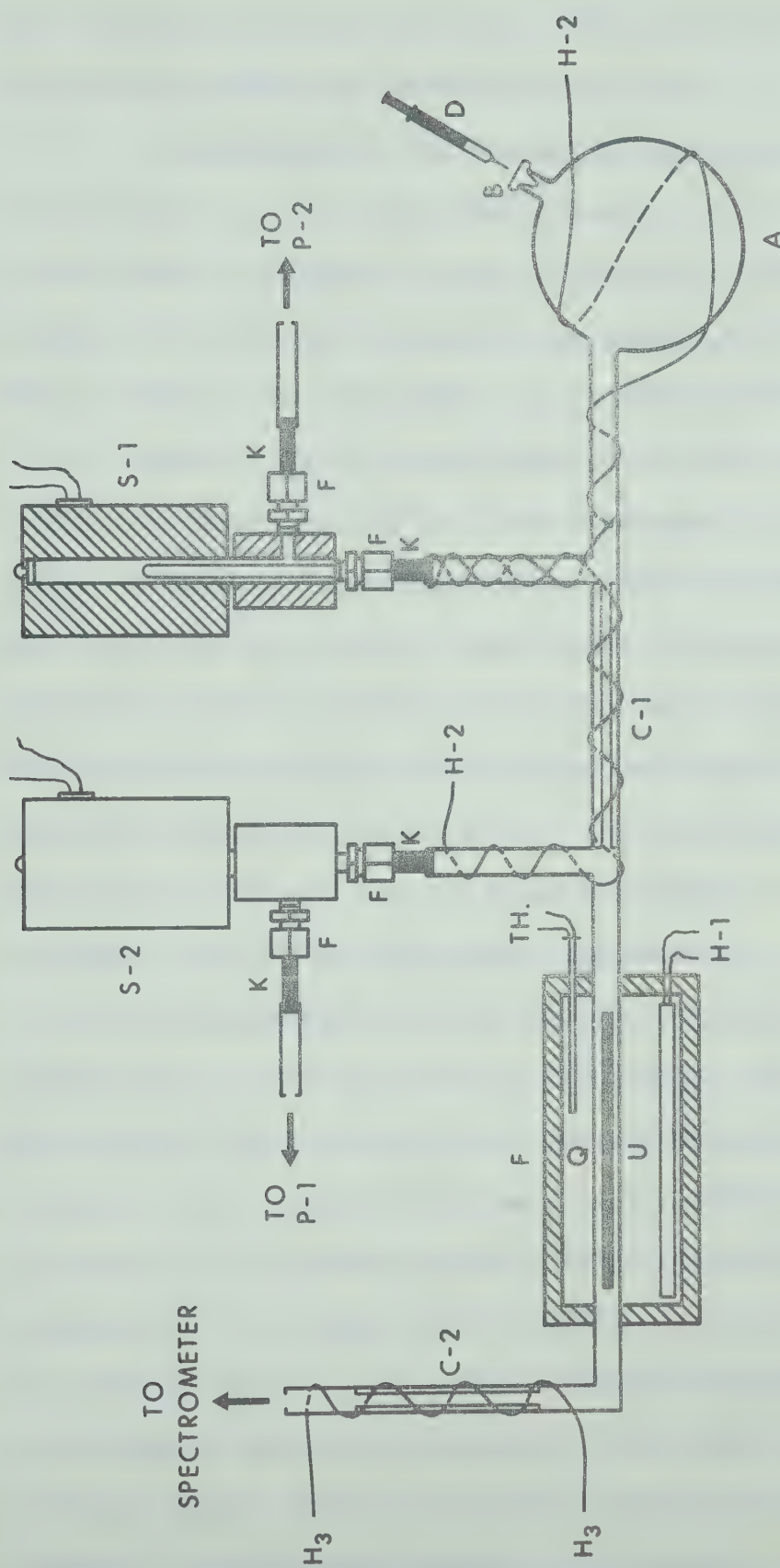


Figure 4.10 INLET SYSTEM FOR SIMPLE HYDROGEN COMPOUNDS

passes through restriction C-1, which is a capillary leak .008 inches by 4 inches to the uranium furnace. The pyrex glass ware and the leak are also heated by the heating tape, H-2.

The heaters for the uranium furnace are two rectangular coils placed in an asbestos lined galvanized box, F. The furnace itself consists of quartz tubing, Q, forming a triple pass over the heater coils. The gas within the tube passes over strips of uranium foil, U, each 0.007 inches thick by 0.2 inches wide by 2.0 inches long. There are six strips employed; two in each pass of the quartz tubing over the heater coils. This triple pass ensures that the vapour is retained long enough to be reduced to hydrogen gas. The gas then flows into the mass spectrometer by passing through a second capillary leak, C-2, which is .02 inches by 2.0 inches in length. This leak slows the flow of gas to the source and helps to ensure that the hydrogen deuterium ratio of the gas is the same as that in the vapour introduced into the expansion vessel. The uranium has different solubilities for hydrogen and deuterium, and so the flow of the reduced hydrogen gas from the simple hydrogen compound must be held up to permit saturation of the uranium metal. The samples are cleared from the source of the mass spectrometer and from the expansion volume by activating two normally closed solenoid valves, S-1 and S-2. The solenoids are all metal stainless steel and are connected to the glassware with Swagelok one-quarter inch fittings, F, connected to Kovar-glass seals. There are two solenoids because of the need to pump the components of the system through separate diffusion pumps. This is to prevent contamination of the source by elements in the hydrogen compounds. For example, if during the

analysis of H_2S , H_2S gets into the source it will decompose and deposit sulphur on the walls and plates of the source and this will contribute to the background level. Eventually the machine would have to be baked out causing unwarranted down time.

The furnace temperature is checked periodically using an iron-constantan thermocouple, TH, with a Leeds Northrup model 8686 potentiometer to obtain the millivolt readings. The values are converted to temperature using a millivolt conversion scale (65). The condition of the uranium is checked visually from time to time. A rise in the pressure in the source to obtain the same size hydrogen peak indicates a rise in background in the source. Scanning the peak related to the compound will give an indication of whether or not the uranium has to be replaced. Limited experience indicates that up to 800 samples can be analyzed before the uranium strips have to be replaced. The uranium is easily replaced by breaking the quartz pyrex joints and replenishing with fresh strips.

G. Automation of Uranium Furnace Samples

To facilitate the handling of large numbers of samples of hydrogen containing compounds, the system was semi-automated. A schematic of the process is shown in Figure 4.11. The most abundant peak of the hydrogen isotopes, mass two, is monitored by attaching a relay mechanism to the output of the vibrating reed electrometer that measures the ion current for mass two. A control relay accurate to 1 part in 10,000 serves the purpose of obtaining a reliable set point. The relay releases when the signal of the electrometer reaches a preset value. Once the hydrogen signal for a sample in the furnace has reached the preset value three relays are

opened. The first activates a solenoid, S-1, this causes the compound before the first capillary leak, C-1, to be pumped away through a waste vacuum line. At the same instant, the digital recorder is activated and prints the I_3/I_2 ratio for the sample, where I_3 is the intensity of mass three and I_2 the intensity of mass two. The method of obtaining the ratio is explained in Section 4.3E. Immediately upon the triggering of the digital printer, a delay timer mechanism is activated. This mechanism controls the period of time that the printer is working. The electrical schematic of the various relays and timers used in this operation is shown in Figure 4.12.

Once the desired printout is obtained, usually 10 to 12 values of the ratio, the delay timer activates three relays. The first shuts off the printer, the second starts another timer and the third activates a second solenoid, S-2. The second solenoid is opened to permit the removal of all traces of that sample from the furnace and source of the mass spectrometer in order to make way for the next sample. The other timer is started to standardize the length of time between samples. The criteria for this period of time is based on the diminished signal of the mass two electrometer. Within four minutes the signal is down to its zeroed reference. At this point a buzzer is sounded to let the operator know that another sample can be introduced. The operator must then press a reset button, that closes the solenoid valves, and resets the timer mechanisms before introducing the next sample. The average length of analysis from time of injection until the sample has been pumped out of the mass spectrometer is 8 to 10 minutes.

For samples of hydrogen-containing compounds that the

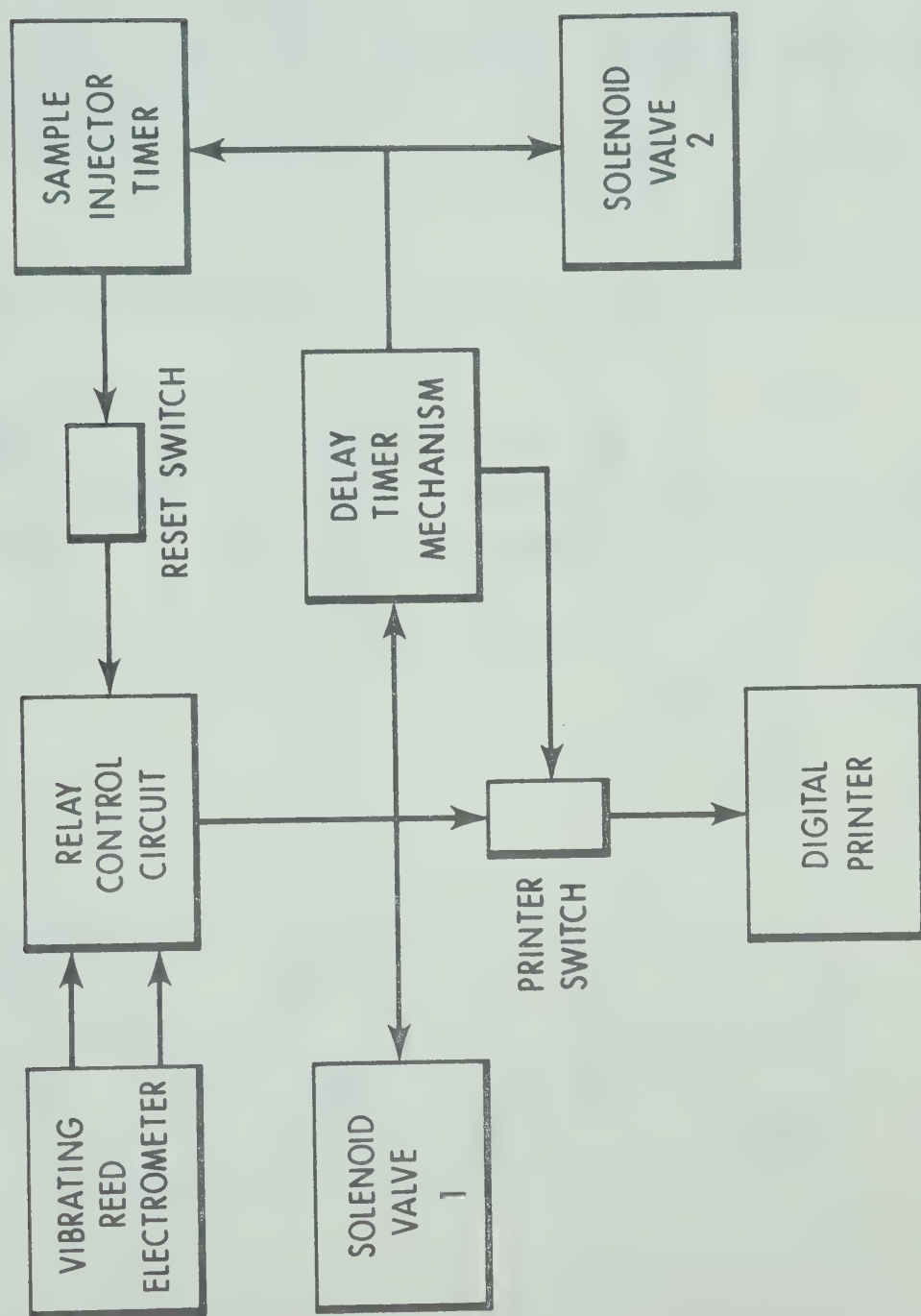


Figure 4.11 SCHEME FOR AUTOMATION OF FURNACE SAMPLES

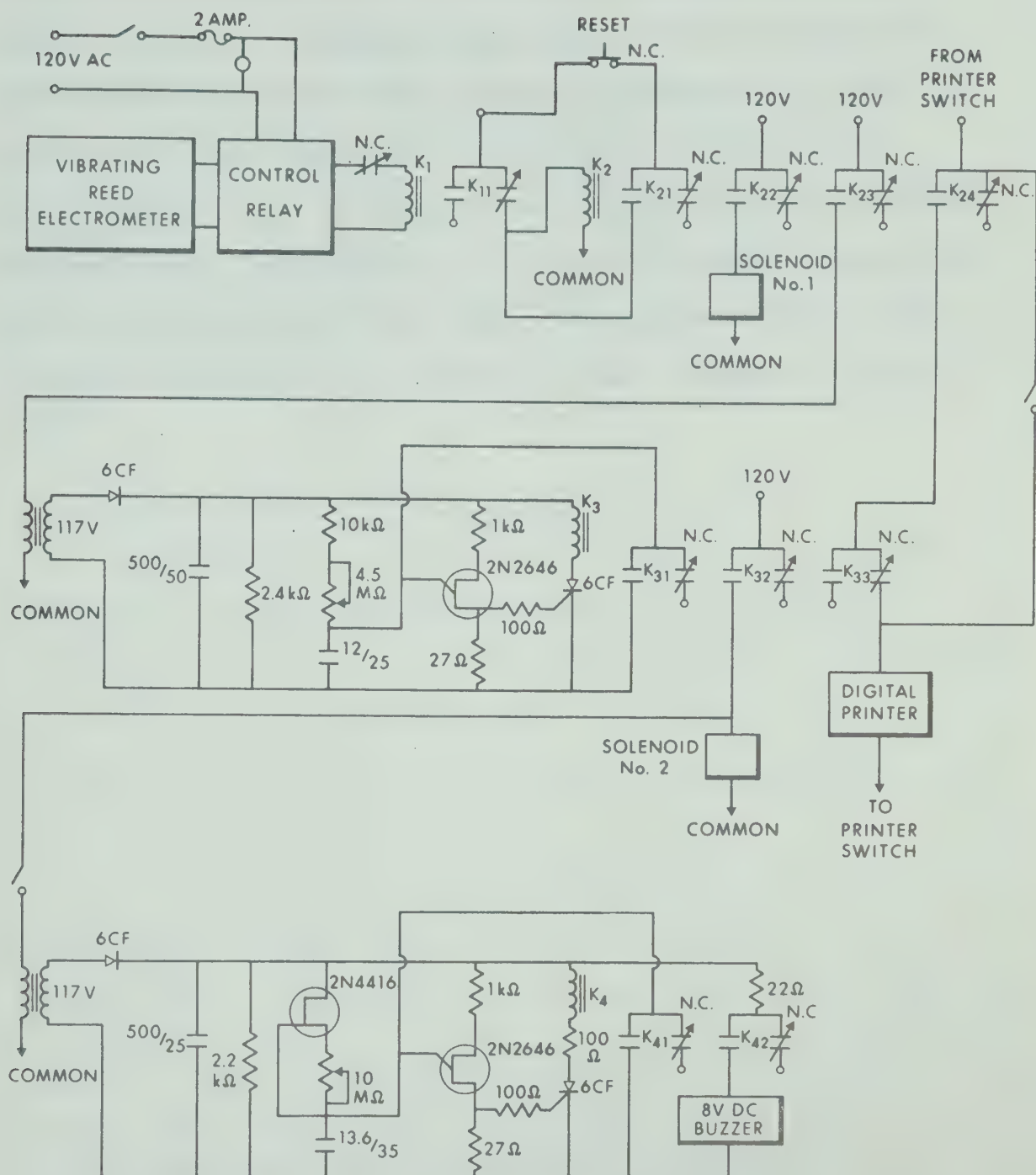


Figure 4.12 CIRCUIT DIAGRAM OF RELAYS AND TIMERS USED FOR FURNACE SAMPLES

isotopic ratio is required, it is necessary to equilibrate these samples with water of a known isotopic ratio. Once the sample has been equilibrated and the water purified in some manner to remove the diffused gas, i.e. remove H_2S by freeze-drying or filtering the water, then this water is placed in the uranium furnace by the method outlined above. The difference in the concentrations of the water is contributed to the sample under study. This prevents the instrument from being contaminated with elemental sulphur, nitrogen, or carbon.

CHAPTER V

RESULTS AND DISCUSSION

The 90° sector mass spectrometer was extensively tested for the analysis of deuterium over a period of six months. Operating procedures have been developed and are outlined in Appendix B. Tests were carried on to determine the performance of the instrument; its stability with time and the repeatability of the analysis for standard samples.

5.1 Detection of Masses Two and Three

The location of the mass peaks of hydrogen and deuterium were acquired from a mass spectrum that was obtained by scanning simultaneously the positive ion current intensities and plotting them against the applied accelerating voltage. A typical scan is shown in Figure 5.1 and depicts the entire spectrum of the instrument for a scanning rate of 200 volts per minute.

As the ion beam moves onto a collector slit, the current measured on the collector increases until the entire beam is within the slit. When the width of the slit is larger than the beam width, the signal stays at a maximum until the scanning voltage is such that the beam leaves the slit. Good resolution of the peaks implies that a peak does not interfere with the peak intensity adjacent to it. The peak shapes observed at the higher voltages are well resolved as seen in Figure 5.1. The sides of the peaks are nearly vertical indicating that the beam is well defined and shaped. The absence of "tails", i.e., sloping peak sides, is an indication that most of the ions have the same energy. The peaks obtained by scanning at the



Figure 5.1 PEAK SHAPES OBTAINED SCANNING AT 200 V/min.

lower voltages have a much poorer resolution. Poor resolution is due in part from one of, or a combination of, the following:

- a) improper alignment of the analyzer magnet
- b) improper focusing of the ion beam in the source
- c) too high a gas pressure in the analyzer tube resulting in dispersion of the ion beam
- d) too wide a slit in front of the collectors
- e) voltage discriminations caused by changing the accelerating potential.

The fact that these higher masses have such poor resolution is of little consequence, since the machine is to be used strictly for hydrogen and deuterium analysis. However, the principle reasons for poor resolution in this case are the wide slits used for the collectors and the voltage discrimination affects that occur because the accelerating potential is varied.

The dual collection scheme requires that the peak for mass three lie within the scan of mass two. Then an operating voltage can be selected which is in the range which gives maximum currents for both masses two and three. For this instrument, the mass three peak is flat and is within the mass two scan over the range of 2900 to 2980 volts. An operating value of 2940 volts was selected.

The peak shapes for masses two and three are very dependent on the position of the analyzer magnet and flat-topped peaks are only obtained when the magnet is in a particular location. The peaks as shown in Figure 5.1 were obtained only after considerable trial and error adjustments were made to the analyzer magnet and to the focusing magnets on the source. The presence of external magnets on the source

increases the emission current, and hence the ionization of the hydrogen gas that has entered the source. The proper alignment of these pole pieces must be made to insure that a maximum emission current, that is, trap current, is obtained from the filament. The peak shapes may also be improved once these magnets are in place by electrical focusing through variations of the potentials applied to the plates in the source. Repositioning of the magnet will be necessary after the instrument has been bodily moved. Similarly, when the source has been adjusted, i.e., replacing burned out filaments, the focusing magnets will have to be readjusted.

Once the maximum intensities of masses two and three have been located, then the ratio of these masses can be obtained for a sample. The error in reproducing the value of the ratio for a sample is of the same order as the error resulting from fluctuation in the vibrating reed electrometers. The noise level of the mass three electrometer is 10 parts in 1,000 whereas the noise level of the mass two electrometer is only 1 part in 1,000. The reason for the differences in noise levels, is that the mass three electrometer operates on a scale that is 1000 times more sensitive than the mass two electrometer. Most of this noise results from vibrations transmitted from the mechanical vacuum pumps through the hose connections. These vibrations bring about movement in the source and hence alter the ion beam. This causes fluctuation to occur in the ratio read out. Additional noise has been successfully removed by increasing the suppression voltage on the collector slits to values in excess of 50 negative volts.

5.2 Contribution of H_3^+ Ion

The presence of H_3^+ ions contribute to the mass three peak and causes an uncertainty in the analysis of the deuterium content of a sample. As stated in Section 3.5 the formation of H_3^+ ions is proportional to the square of the pressure. The pressure within the source is kept fairly low during the analysis of a sample, for example, the normal pressure is 2×10^{-6} mm of Hg; at this pressure quite adequate signals for the masses two and three are obtained. In determining the amount of signal due to H_3^+ production, the ratio, R , that is I_3/I_2 , is plotted against I_2 and the straight line is extrapolated back to a zero signal I_2 to obtain R_0 . The ratio, R_0 , the intercept, is chosen as the value due to deuterium, plus any secondary effects and a measure of H_3^+ production is simply $(R - R_0)/R_0$.

Water containing 130.5 ppm deuterium was analyzed and the I_3/I_2 ratio is plotted versus I_2 on Figure 5.2. Different values of I_2 are obtained by varying the system pressures. The intercept is 125.0 and differs from the expected value because of secondary effects that vary from day to day. The measure of H_3^+ production $(\frac{R}{R_0} - 1)$ is plotted on Figure 5.3 along with H_3^+ contribution that other researchers have attributed to their instruments (13,14,15,66).

The contribution of H_3^+ to the mass three peak due to pressure is approximately ten percent at a mass two current intensity of 30×10^{-10} amperes. This is slightly higher than the values claimed by Nief and Botter (13) and Bigl (15).

By applying different voltages to the repeller to make the repeller more negative than the case, different amounts of H_3^+ are obtained at a given system pressure. Figure 5.4 is a plot of the

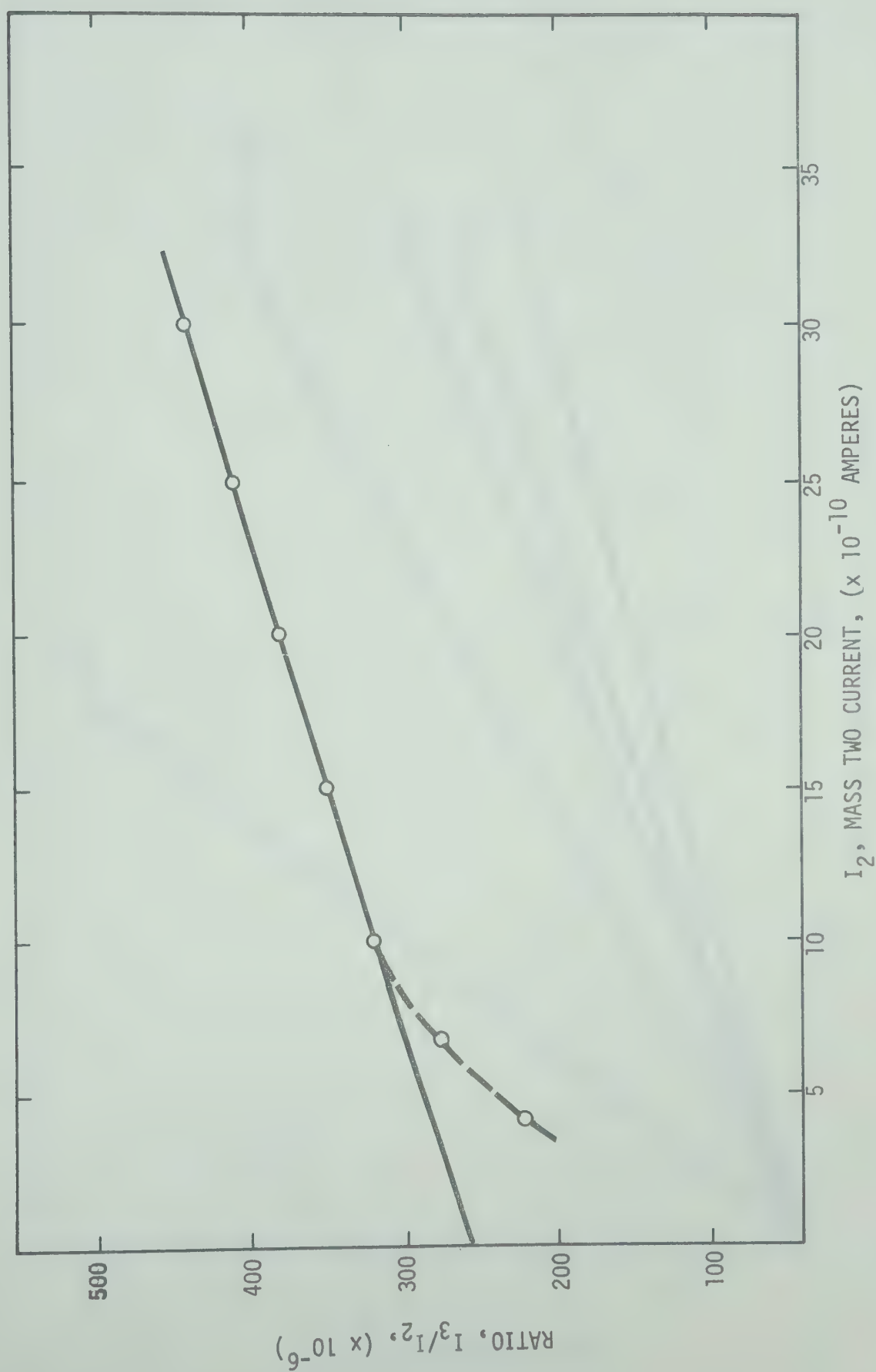


Figure 5.2 PRESSURE DEPENDENCE OF I_3/I_2 RATIO OF A SAMPLE CONTAINING 130.5 PPM FOR A REPELLER VOLTAGE OF -35 VOLTS

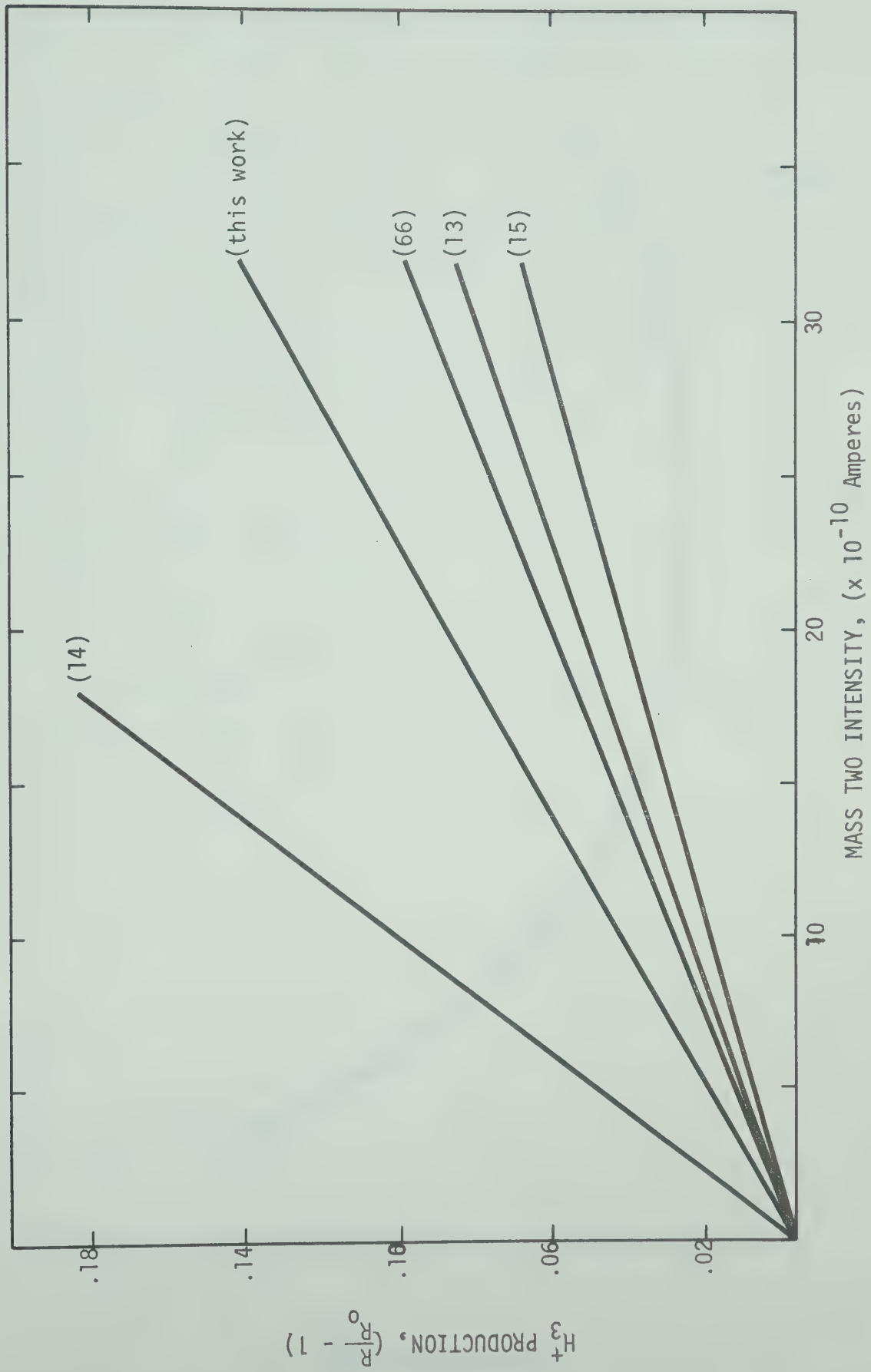


Figure 5.3 H_3^+ PRODUCTION FOR HYDROGEN DEUTERIUM INSTRUMENTS

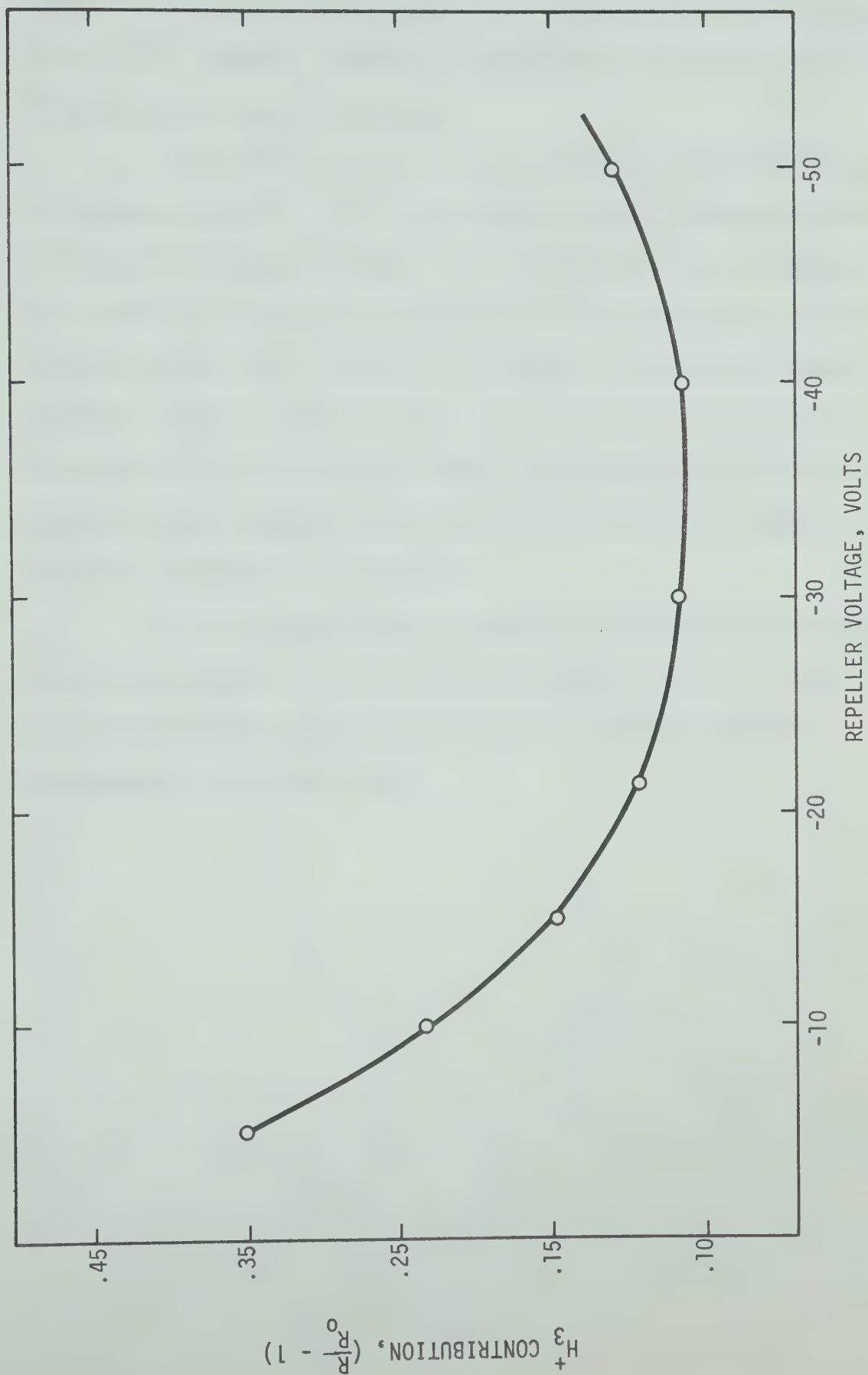


Figure 5.4 H_3^+ PRODUCTION VS CHANGES IN REPELLER VOLTAGE AT CONSTANT I_2

contribution of H_3^+ versus applied voltage to the repeller for a sample containing 130.5 ppm deuterium at a mass two current intensity of 50×10^{-10} amperes. Minimum H_3^+ production is obtained at 35 volts negative with respect to the case.

The effects on the trap current for the same conditions are plotted as Figure 5.5. The trap current reaches a maximum value at the repeller voltage for which minimum H_3^+ production is obtained. The reduction of the trap current results from a deflection of the electron beam, which is negatively charged, by the higher negative potential applied to the repeller plate. Since the total emission current rather than the trap current is regulated, the total emission current remained constant throughout the change in the repeller voltage, as observed in Figure 5.5.

On the diagrams shown previously it should be noted that the H_3^+ contributions are not constant. These are typical results and the operating experience has shown that the H_3^+ production increases as the filament ages.

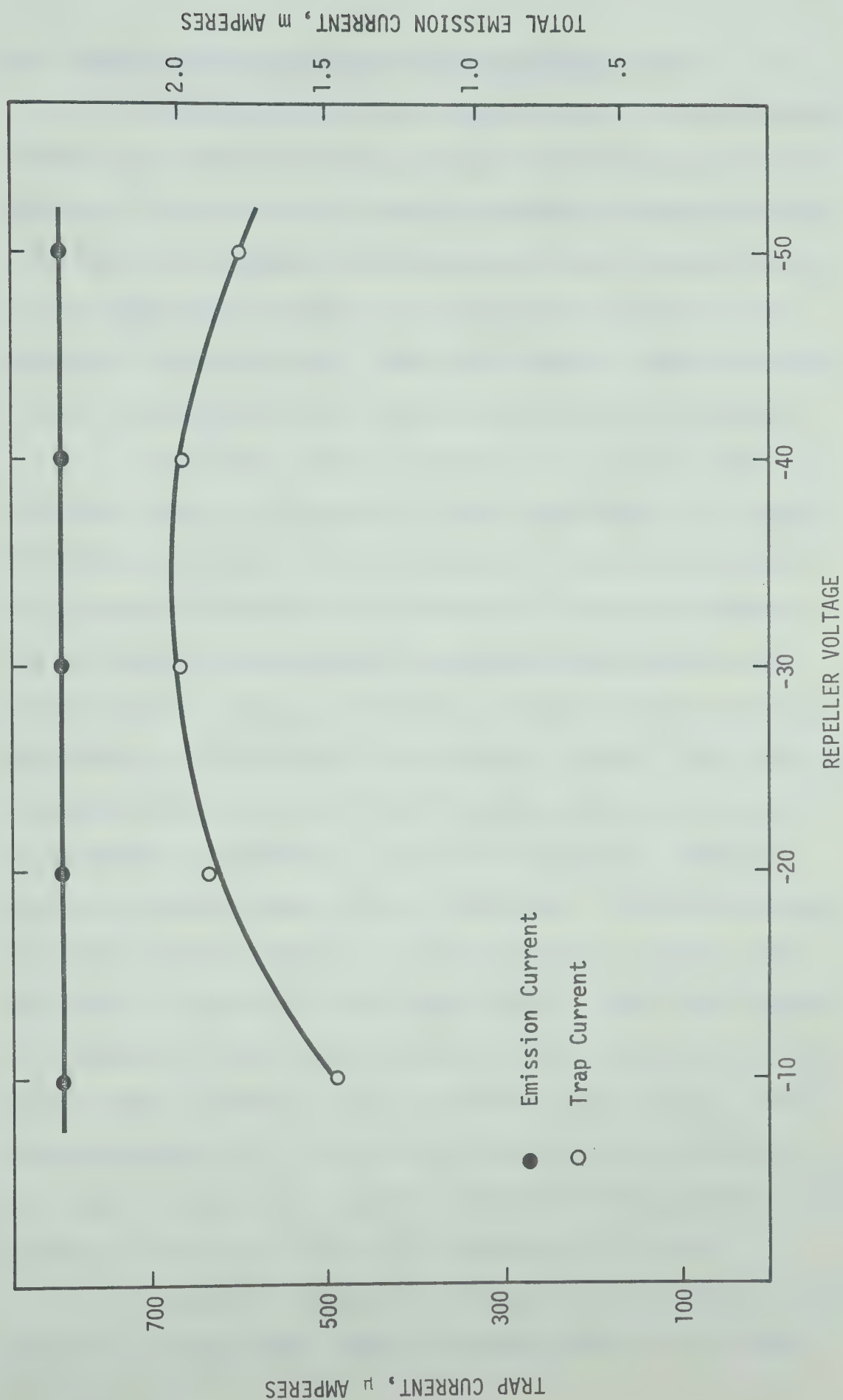


Figure 5.5 CURRENT CHANGES DUE TO REPELLER VOLTAGE

5.3 Determination of Absolute Deuterium Concentration

The determination of the absolute values of deuterium concentration is difficult not only because of the H_3^+ ions, but also because of the presence of a number of secondary effects which cause additional uncertainties. These secondary effects include changes in the power supply voltages and irregularities in the ion beam production from day to day. These effects make it almost impossible to obtain an absolute value from the analysis of a single sample.

Such effects can be accounted for by employing reference standards, that is, calibrating the mass spectrometer with samples of known composition. The determination of the absolute analysis of an unknown by measuring the difference in composition between a set of standards and an unknown assumes that the standards have correct absolute values. In this work, standards were obtained by the addition of heavy water to a principal standard. These artificial standards along with the principal standard were analyzed by Chalk River Nuclear Laboratories. The principal standard, Edmonton tap water, was found to have a value of 130.5 ppm. The other standards had values of 145.2; 158.0; 171.0 ppm respectively. These values are based on Standard Mean Ocean Water (SMOW). Chalk River compared our standards to their working standards whose values had been compared to NBS-1 and NBS-1a which are international standards. The reported uncertainty in Chalk River analysis of our standards was ± 0.2 ppm. The principal standard is protected from contamination by storing it in a special three litre stainless steel vessel.

The procedure followed in order to obtain deuterium concentrations in unknown water samples requires knowing the deuterium

value of three samples, i.e. reference standards, over the range for which the analysis is desired.

1. The actual values of two of the standards are compared to the principal standard, obtaining the relative abundance of deuterium, δD_{St} , for

$$\delta D_{St} = \left(\frac{C}{C_{St}} - 1 \right) 1000 \quad 5.1$$

where $C [=]$ the value of the enriched standard, ppm

$C_{St} [=]$ the value of the principal standard, ppm

2. These standards are then analyzed on the instrument to obtain the relative abundances, δD_I , for

$$\delta D_I = \left(\frac{R}{R_{St}} - 1 \right) 1000 \quad 5.2$$

where $R [=]$ ratio of measured beam intensities of

masses two and three of the unknown sample

$R_{St} [=]$ ratio of measured beam intensities of

masses two and three of the principal standard

3. The values of δD_{St} , δD_I obtained for the standards are then plotted against each other.
4. Then, the unknown is analyzed and its abundance, δD_I , relative to the principal standard is obtained.
5. The value of δD_{St} for the unknown is obtained from the plot, and the concentration calculated using equation 5.1.
6. A particular calibration is useful for as long as the

instrument is fully operational, i.e., filament and high voltage left on continuously.

The reliability of the procedure is illustrated by the following example where one of the standards A-3 is treated as an unknown. The pertinent values of δD_{St} and δD_I are given in Table 5.1. Figure 5.6 is a plot of δD_{St} versus δD_I and the value of δD_{St} for the unknown is obtained from this figure as 210. The deuterium concentration as calculated from equation 5.1 is 157.9 ppm. This compares to the value of 158.0 ppm which was obtained at Chalk River.

A measure of the reproducibility or precision of the instrument is shown by the results given in Table 5.2. These were obtained over a period of two months.

The procedures outlined above can also be applied to the analysis of gas samples. An approximate value can also be obtained by plotting I_3/I_2 versus I_2 and extrapolating to zero pressure. Such a plot for a gas sample containing approximately 650 ppm is shown in Figure 5.7. The intercept gives the value of the ratio HD/H_2 . To obtain the deuterium concentration, this ratio must be halved. The deuterium content obtained in this is 690 ppm.

TABLE 5.1
MEASUREMENTS FOR ABSOLUTE VALUES

Sample	ppm Chalk River	δD_{St}	δD_I	δD_{St} From Graph	ppm Calculated
A-1 (Principal Standard)	130.5	0.0	0.0	-	-
A-2	145.2	112.6	113.1	-	-
A-4	171.0	310.3	342.4	-	-
A-3 (Unknown)	158.0	-	231.3	210	157.9

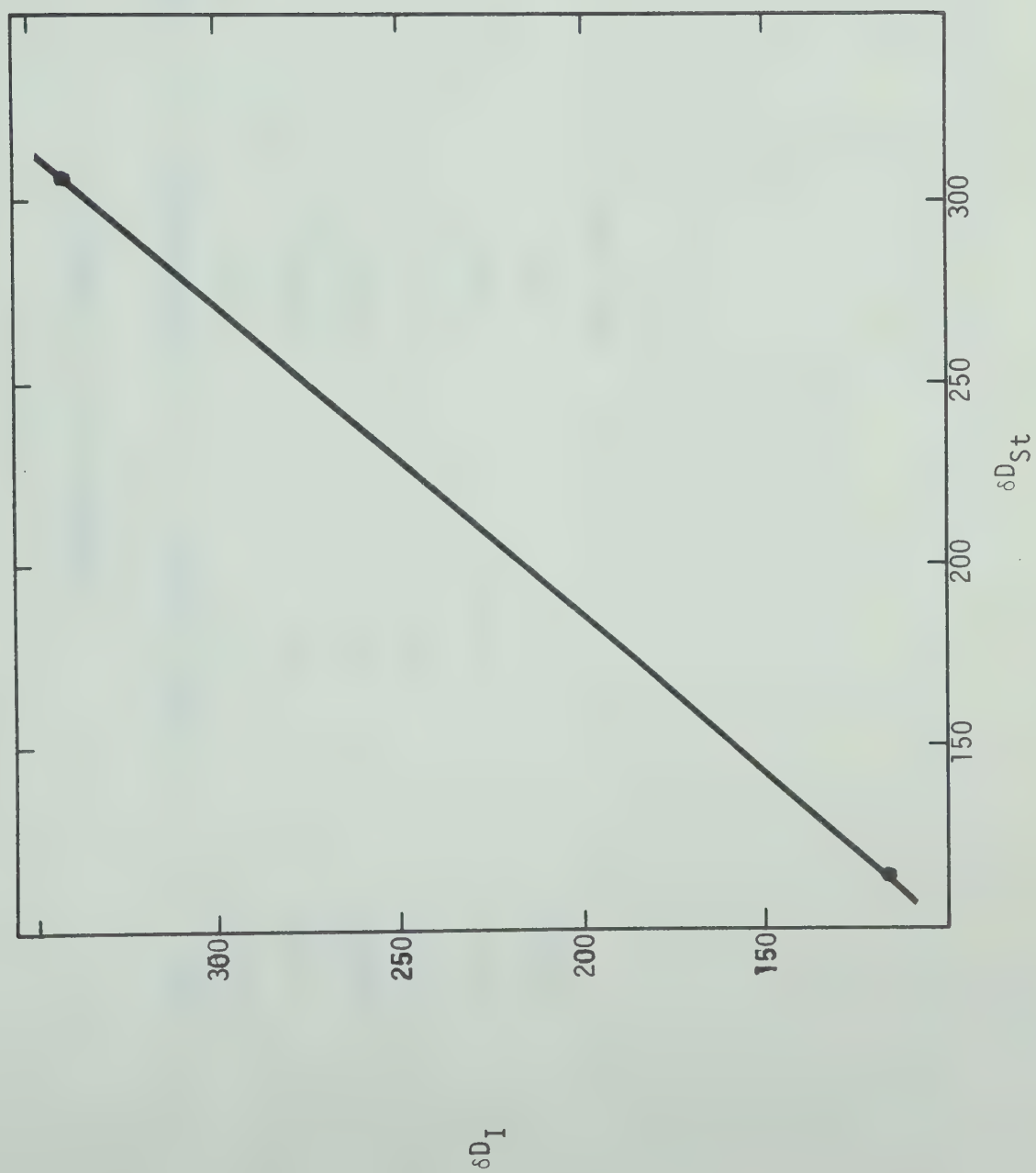


Figure 5.6 ACTUAL ABUNDANCE VS MEASURED ABUNDANCE

TABLE 5.2

REPRODUCIBILITY OF ANALYSIS

Date	Sample Analyzed	Calculated ppm	Deviation ppm
26/2/71	A-3	158.8	+ 0.7
3/3/71	A-3	158.7	+ 0.6
16/3/71	A-3	157.5	- 0.6
21/3/71	A-3	157.3	- 0.8
2/4/71	A-3	158.6	+ 0.5
15/4/71	A-3	157.9	- 0.2
		Avg. 158.1	Avg. \pm 0.6

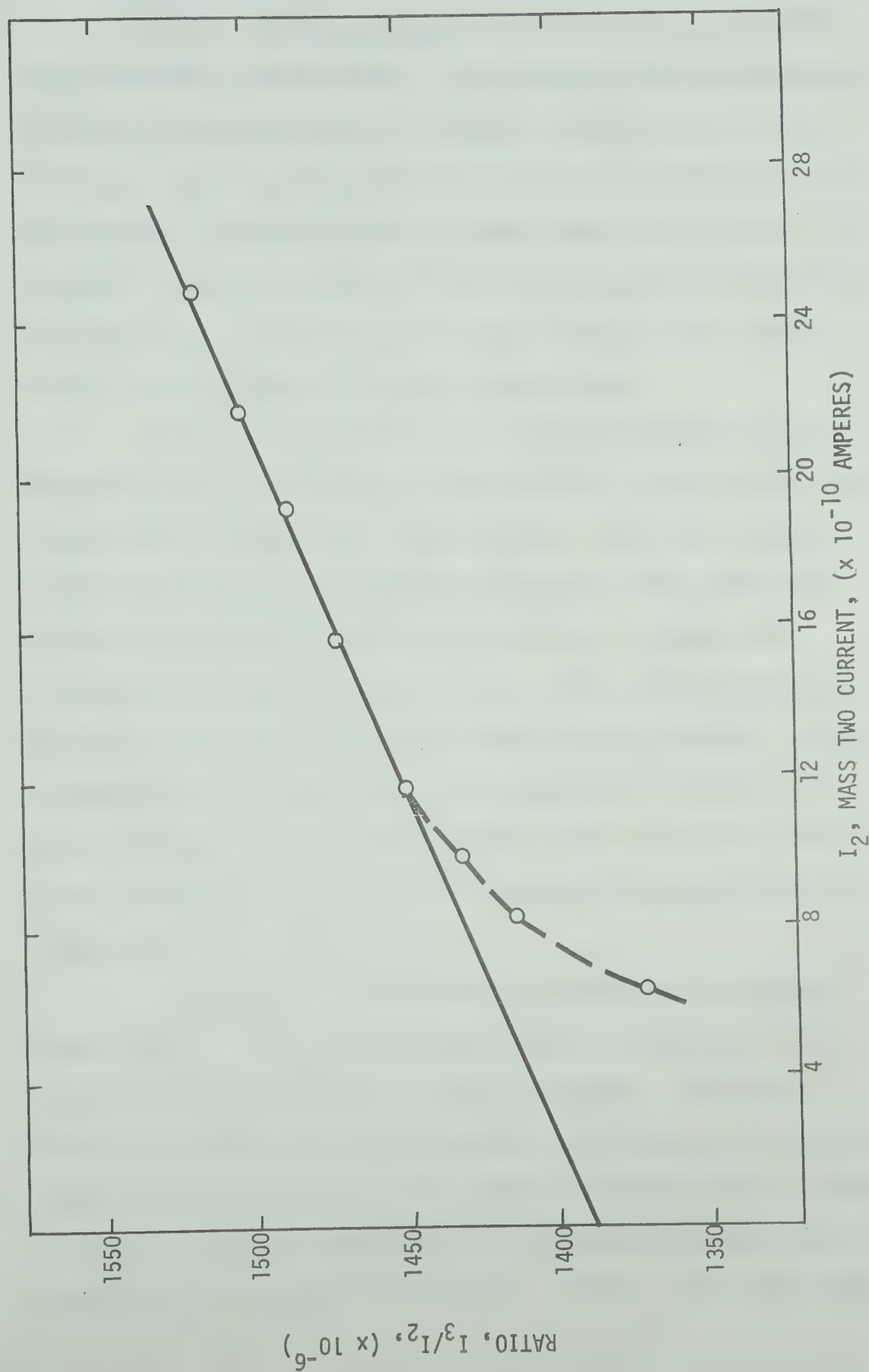


Figure 5.7 GAS SAMPLE ANALYSIS FROM EXTRAPOLATION

5.4 Memory Effects

Memory effects were apparent when analyzing gas samples that differed by more than 20%. These resulted from switching from standard to unknown and back to standard using the glass solenoid valves, in that the dead space between each valve system could not be completely evacuated before the other sample was introduced. As a result, there was a mixing of the residual gas and the gas being introduced, and this led to a subsequent change in the isotopic ratio of the two gases that were being analyzed.

These mixing effects can be reduced by taking more time between samples, or by using a standard that is fairly close to the value of the unknown that is being analyzed. More time between samples will allow a more complete evacuation of the dead space. This leads to greater waste of gas samples but increases the reliability of results. However, this is also time consuming and the rapid valve system is no longer used in an optimum way. Using a standard that is quite close to the unknown will minimize the mixing effects which will then be of the order of the noise level of the instrument. However, this requires having a predetermined idea of the value of the unknown.

Slight memory effects were also present when analyzing water samples. This was overcome by injecting samples until the analysis was constant between successive samples. For samples that were separated by large differences, eg. 20 ppm., five injected samples were enough to completely remove the memory effects. Memory effects were characterized by using the formula presented by Nief and Botter (13) and given in Table 5.3. Table 5.3 shows the memory

effects found when analyzing three samples differing from each other by approximately 15 ppm. Memory effects are due to residue water left in the waste lines between samples. These effects were reduced by heating the glassware to 100°C.

TABLE 5.3
MEMORY EFFECTS

Sample	Run Number	I_3/I_2 $\times 10^{-6}$	Memory	Accuracy
Tap water	1	328.2		
130.5 ppm	2	327.5		$\pm .15\%$
	3	327.8		
	4	327.3		
A-1	1	361.7	5%	
145.2 ppm	2	363.5	3%	
	3	364.0	1.6%	145.4 \pm .7 ppm
	4	364.6	-	
	5	364.8	-	
A-2	1	394.4	7.5%	
158.0 ppm	2	395.2	5%	
	3	395.8	3%	$\pm 158.1 \pm .6$ ppm
	4	396.8	-	
	5	396.7	-	

$$\text{Memory effects} = \frac{R_N - R_F}{\Delta R}$$

where R_N = measured value of n^{th} sample

R_F = measured value of final sample

ΔR = difference in values of present sample and previously different sample, i.e. A-1, and A-2.

5.5 Detection of Compound Peaks

An increase in pressure without a corresponding increase in the mass two signal indicated a reduction in the efficiency of the uranium and a check on the H_2O^+ peak generally confirmed the need for renewal of the uranium foil. Monitoring the water peak is a convenient means of detecting when the uranium foil is no longer able to completely reduce water samples. A scan obtained at 50 volts per minute is shown in Figure 5.8 and shows the presence of carbons, nitrogens, oxygens and water. Normally, these peaks are all residual peaks, they do not increase with increasing hydrogen gas pressure in the source and thus are constituents of the background of the instrument. These peaks are not resolved for reasons stated in Section 5.1. However, the water peak is sufficiently resolved to be useful for the detection of the depletion of uranium. As a guide the peaks are observed only after 100 samples are analyzed. Limited experience indicates that 800 samples can be analyzed before the uranium foil must be replaced.

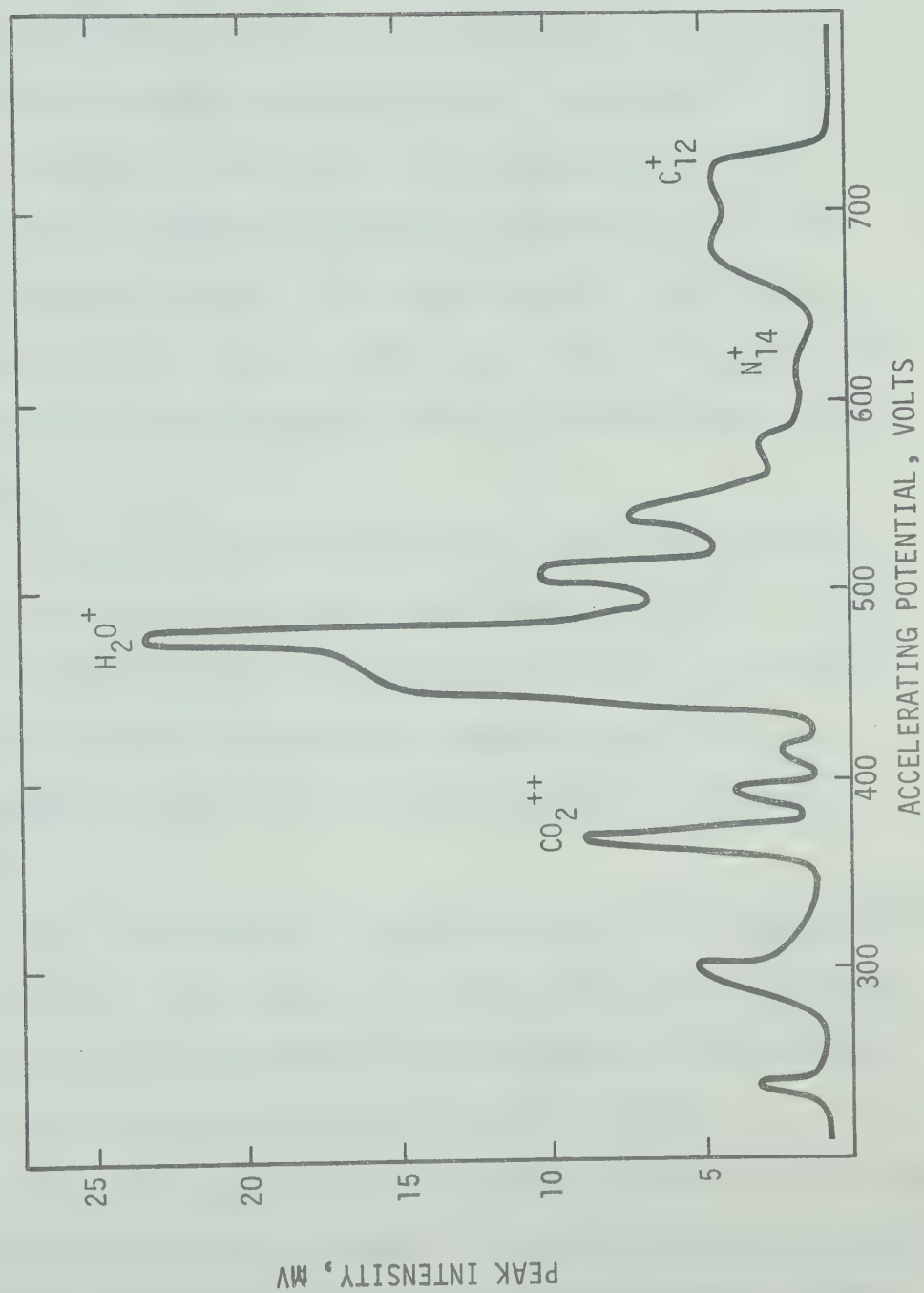


Figure 5.8 THE LOCATION OF THE H_2O PEAK BY SCAN ON THE MASS THREE COLLECTOR

CHAPTER VI

CONCLUSIONS

A 90° sector mass spectrometer employing dual collection which can be used for the analysis of deuterium at low concentrations in simple hydrogen compounds has been constructed.

A method of analysis has been demonstrated whereby absolute deuterium concentrations can be determined to ± 0.6 ppm at natural abundance levels. This method requires the use of at least three standards. Memory effects are minimal through the use of heating tapes and high capacity mercury diffusion pumps on the sample lines.

The use of a repeller electrode in the source permits the use of high operating pressures and reduces the H_3^+ ion contributions. The amount of H_3^+ ion production varied with the pressure. In the range in which the machine was operated, the H_3^+ ion production amounts to some 10% of the total intensity of the mass three peak.

The incorporation of a uranium furnace in the sample inlet system permits the rapid analysis of water samples and should make the direct analysis of deuterium in other hydrogen containing compounds, such as NH_3 , H_2S and aliphatic amines possible.

The capital cost for the instrument including all electronic components was approximately \$16,000. The major costs are: digital equipment on loan \$7,000, two vibrating reed electrometers \$4,000, high vacuum components \$2,500, remaining electronic equipment \$1,500, and materials of construction and support equipment \$1,000. The

cost could be reduced by replacing the digital equipment with a teletype terminal which would link the outputs from the vibrating reed electrometers directly to the department's IBM 1800 computer.

The mass spectrometer could be improved by the use of an electromagnet and an emission regulator that would regulate only the trap current. The use of an electromagnet would give better resolution to ion beams of higher mass, making the instrument slightly more versatile. However, the additional cost is not warranted for the intended applications. With the present emission regulator, the total emission current remains constant while the trap current changes when the repeller voltage is varied. Ideally, the trap current should remain constant for easier operation and "tuning" of the peak shapes. The instrument has shown that it can perform well without these alterations and they would only improve the convenience of operation.

A final recommendation to facilitate the analysis of gas samples would be to join the gas reservoirs to the furnace leak. This would enable hydrogen gas and water vapours to pass through the same leak, and would remove the necessity of having to store gas standards, as liquid standards could then be used when analyzing gas samples.

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APPENDIX A
BASIC DESIGN EQUATIONS

A.1 The Mass Spectrometer Equation

The mass spectrometer equation

$$\frac{m}{e} = \frac{r_m^2 B^2}{2V} \quad \text{A.1.1}$$

can be used to calculate the ion beam path, r_m , when a particular species is subjected to an accelerating voltage, V , in a magnetic field of strength, B .

m [=] mass of species examined, kilograms

e [=] electron charge of ion, coulombs

B [=] magnetic field strength, gauss

r_m [=] radius of ion path, meters

V [=] acceleration potential, volts

changing to a more convenient form by defining

M [=] mass of species, atomic mass units

e [=] number of electronic charges

R [=] radius of ion path, centimeters

$$\frac{M}{e} = 4.83 \times 10^{-5} \frac{B^2 R^2}{V} \quad \text{A.1.2}$$

For a given mass spectrometer in which the radius is usually fixed, this equation is utilized to determine the mass of the species collected. The mass to charge ratio, M/e , becomes the mass of the species scanned when the species is singly charged.

A.2 Collector Placement

In a dual collection scheme, the collectors must be positioned so as to be able to detect both signals at their highest

intensity and yet avoid the signal from one beam adding to the intensity of the other. For a symmetric analyzer the dispersion of the ion beams as they travel first through an accelerating potential and then through a magnetic field, is given by (64)

$$D = \frac{R\Delta M}{M} \quad \text{A.2.1}$$

where

$D [=]$ dispersion measured perpendicular to a centrally focused beam, inches

$R [=]$ radius of curvature of the ion path, inches

$\Delta M [=]$ difference in mass of the ions under consideration, amu.

$M [=]$ mass of the primary focused ion, amu.

For the collection of masses two and three

$$\Delta M = 1, \quad M = 2, \quad R = 2.50 \text{ inches}$$

$$D = \frac{2.5(1)}{2} = 1.25 \text{ inches}$$

The required spacing of the slits was made to conform to this setting in order to prevent ions destined for the mass two collector from entering the mass three collector. Guards between the collectors were also used to prevent the flow of ions.

A.3 Determination of Furnace Leak Size

When the initial pressure of the sample is very low, the corresponding mean free path of the molecules is much larger than the effective diameter of the leak opening, and the probability of inter-molecular collisions within the leak is small compared to the

probability of molecules colliding with the walls. The condition where each molecule proceeds through a leak individually is termed molecular flow.

The laws of molecular flow were derived by Knudsen in his work on the flow of rarefied gases through tubes and small openings. Defining Q_m as the time rate of change of the pressure-volume product, which at unit pressure becomes equal to the volume, V , of gas discharged per second from a capillary tube, the Knudsen equation for cylindrical tubes may be written as (78):

$$Q_m = \frac{d(\bar{p}V)}{dt} = 3800 \left(\frac{D_T^3}{L} \right) \left(\frac{T}{M} \right)^{1/2} (p_1 - p_2) \quad \text{A.3.1}$$

where

D_T [=] diameter of tube, cm

L [=] length of tube, cm

T [=] temperature, °K

M [=] molecular weight of gas

p_1 [=] pressure at high side, mm

p_2 [=] pressure at low side, mm

\bar{p} [=] mean pressure, $\frac{p_1 + p_2}{2}$, mm

Consider a sample of 10 μ L of water injected into a one litre reservoir which is at a temperature of 100°C, the pressure, p_1 , will be 13 mm of mercury.

The pressure in the mass spectrometer will be 10⁻⁷ mm of mercury so that the mean pressure will be 6.5 mm of mercury. In order to keep fractionation effects constant, the reservoir should not be depleted at a very fast rate, thus if a loss of 2% per

hour in the reservoir pressure is used as a guideline to prevent fractionation effects from occurring the gas flow rate becomes

$$Q_m = .0361 \text{ litre-mm/sec.}$$

for this flow rate, a leak of length 100 millimeters will have to have a diameter

$$D_T = .2 \text{ mm or } .0079 \text{ inches}$$

APPENDIX B
OPERATING PROCEDURES

B.1 Startup from Complete Shutdown

The steps should be followed in the exact order in which they are placed in this manual. Difficulties may arise, such as poor vacuum, burnt out filaments, etc., if they are not adhered to.

1. General Preparation

(a) open the glass solenoid valves by turning control rheostat to "90", and placing switch in "ALL 4" position.

(b) open the all-metal bellows valve between ion pump and mass spectrometer body, then the Nupro "waste" and "sample" valves.

(c) turn on mechanical pump - "Pump - 1".

(d) turn on mechanical pump - "Pump - 2" after air is pumped out of "pump - 1" system.

(e) wait five minutes then check with tesla coil as close to the diffusion pump exits as possible - operate tesla coil to obtain sufficient spark.

Deep purple - pumps not drawing vacuum or massive leak to Red

Light blue - system is reaching vacuum available by mechanical pumps.

(f) fill liquid nitrogen traps if good vacuum indicated by tesla coil.

(g) shut Nupro "waste" valve - separates two diffusion pumps.

(h) turn on diffusion heater switches - turn rheostats to 20 volts.

(i) wait 1/2 hour, turn rheostats to 30 volts.

(j) wait 2 hours, turn to 45 volts.

(k) wait 2 hours, turn to 65 volts maximum.

2. Ion Pump Startup

(a) use tesla coil as in A(e) above.

(b) switch to "start" on ion pump controls.

(c) close nupro "sample" valve.

(d) push red "on" button. This starts the ion pump and causes it to warm up. 5-10 minutes of warmup are necessary before ion pump becomes functional.

(e) turn selector on ion pump controls to "KV", kilovolts.

(f) once past 4 kilovolts, ion pump is now working, switch scale to "log". When in this position ion pump is in the protect mode. If the vacuum for some reason decreases to 10^{-4} mm of mercury, the pump will shut off.

(g) move switch from "start" to the "protect" position.

3. Filament Conditioning

(a) after three hours of ion pump operation, open "sample" nupro valve. The pressure should remain constant, this can be seen by observing the "log" scale on the ion pump controls.

(b) using the emission regulator, turn filament current on to 2 amperes.

(c) hold in this position for a few hours or until the vacuum is down to 10^{-6} mm of mercury.

(d) turn up filament current to 3 amperes and hold until vacuum reaches 10^{-6} mm of mercury.

(e) turn to 3.5 amperes until vacuum reaches 5×10^{-7} mm of mercury.

(f) turn to 4.0 amperes and leave until vacuum again reaches 5×10^{-7} mm of mercury.

(g) finally, turn the filament current fully on, in this position the filament current will have a value of 4.5 amperes.

The last four steps may take a few hours or up to two days if the filament is new.

4. Electrical Warmup

(a) the trap current on the emission regulator should exceed 800 μ A. The meter reading has a multiplication factor of two (i.e. 800 μ A \equiv 400 μ A on meter). If the current does not exceed 800 μ A, realign the source magnets until it is.

(b) turn the electrometers on by following the instructions of Section D.5 and do the zero check.

(c) turn the high voltage supply to "standby" from the "off" position.

5. Evacuation of Inlet Systems

(a) close the "sample" nupro valve.

(b) evacuate standard and unknown toepler pumps opening the three-way valve to the mercury diffusion pumps.

(c) close the glass solenoid valves by turning the rheostat to "0 volts" but leave the switch in the "all 4" position. This isolates the metal part of the system from the glass diffusion pumps.

(d) evacuate the furnace lines through the diffusion pumps by opening the metal solenoid valves using the "red" switch on the solenoid control board. Press the "reset" button to close the solenoids.

(e) the rheostats for the glass solenoid control can then be turned up to "80 volts". Observe the vacuum gauge, i.e. the "log" scale on ion pump controls, if the vacuum deteriorates shut off the solenoids and wait about five minutes to give the diffusion pumps time to evacuate the system.

(f) repeat (e) until vacuum no longer deteriorates.

B.2 Startup and Procedures for Gas Analysis

(a) make sure that all the glass solenoids are in the open position as in B.1.5(e).

(b) filament should be on as in B.1.3.

(c) turn the high voltage supply from "standby" to "on".

(d) turn the selector switch from " -ve charge" to "+ current" on the vibrating reed electrometers.

(e) turn on the voltage-to-frequency converter.

(f) turn on digital voltmeter.

(g) wait 30 minutes for electronics to stabilize.

(h) fill the toepler pumps with samples while waiting.

Connect the sample bomb to the § joint. Evacuate the dead space between the valve on the sample bomb and the valve to the reservoir. Take a "cut" of the sample by turning the valve on the bomb and introducing a small quantity to the space between the two valves. Now this part of the sample can be let into the reservoir.

(i) zero calibrate the voltage-to-frequency, see Section B.5.

(j) zero calibrate the electrometers, see Section B.5.

(k) introduce samples to the source in the following manner:

(1) turn switch on glass solenoid valve controls from "all 4" to "2 only".

(2) open both three way valves so that gas in the reservoirs is released to the leaks.

(3) introduce "s - standard" or "x - unknown" gas to the mass spectrometer by moving the dial

switch on the glass solenoid controls to "S" from "WW". Turn on digital printer "power" switch.

- (4) turn the function switch to "voltage number 2" and obtain a printout of this signal. This is the mass peak height for hydrogen.
- (5) turn dial switch on glass solenoid control to "X" from "S".
- (6) move the height of mercury in the toepler pump containing "X" until the signal for the mass two peak is equal to the value for "S".
- (7) turn dial switch to "S" from "X" to make sure signal has not changed. If it has, adjust until signal has the same value as before. By keeping a good supply of gas in the reservoir, usually 6 to 8 inches between the mercury and the check valve on the top of the reservoir will suffice, the signal should not change in value.
- (8) once these signals are equalized, turn function switch to "Ratio 1/2" and print out results for "S". Turn dial control to "X" and print out the value.
- (9) these are the values of "R", the isotope ratios of each of the gas samples. Following Section 5.3, a deuterium value can then be found for the unknown sample.

B.3 Startup and Procedure for Furnace Samples

- (a) filament current should be shut off.
- (b) close the glass solenoids, rheostat is turned to "zero". This isolates diffusion pumps from mass spectrometer source.
- (c) open metal solenoids, use the "red" switch on the solenoid control board. This removes air from furnace lines.
- (d) turn on furnace heaters by opening rheostat to "50%" maximum.
- (e) turn on heating tapes to "40%" for reservoir tape and "60 volts" for glassware tape.
- (f) open glass high vacuum line on furnace line between nupro "sample" valve and the furnace.
- (g) turn off metal solenoids by pressing "reset" button on solenoid control board.
- (h) wait 30 minutes for heaters to warm up glassware.
- (i) turn the filament current back on.
- (j) turn the high voltage supply from "standby" to "on".
- (k) turn the selector switch from " -ve charge" to "+ current" on the vibrating reed electrometers.
- (l) turn on voltage-to-frequency converter.
- (m) turn on digital voltmeter and printer.
- (n) wait 30 minutes for electronics to stabilize.
- (o) zero calibrate voltage-to-frequency converter, see Section B.5.
- (p) zero calibrate the electrometer, see Section B.5.
- (q) introduce samples to the source in the following manner:

- (1) set point on solenoid control board should be set so that printer is activated after signal on electrometer from mass two peak is greater than $1/2$ the scale reading. This insures adequate signal for the mass three peak. Do not change this set point for remainder of samples taken.
- (2) introduce sample with syringe not sample size and time required to reach set point, if time too slow, i.e. 10 minutes, increase sample size. If time too fast, i.e. 2 minutes, decrease sample size. Usually around 4 μ l are required.
- (3) after signal is attained and printer activated, the sample will be flushed out of system.
- (4) function switch should be set at "voltage 2". After sample pumped away, sample introduction time is set to sound buzzer when the signal from mass two, i.e. signal viewed on voltmeter reaches zero. If not, set timer to do so. This sets the minimum time between samples, so that furnace has an adequate time under vacuum.
- (5) turn function switch to "Ratio $1/2$ ".
- (6) press reset button and start analyzing samples.
- (7) find deuterium content, by following Section 5.3.

B.4 Shutdown Procedures

Daily

(a) turn off all electronic equipment, including heaters for furnace if on except for

(1) the high voltage supply should be turned from "on" to "standby".

(2) leave filament current on if running a batch of samples that requires only a few days.

This requires only one calibration to be made for standards.

(3) leave on ion pump and diffusion heaters.

(b) make sure liquid nitrogen traps are filled.

(c) close glass solenoid valves by setting rheostat to "zero".

Maintenance

(a) follow daily shutdown procedure including the following

(1) shut off diffusion heaters, remove liquid nitrogen traps.

(2) close the all metal bellows valve to the ion pump.

(3) turn off filament supply.

(b) allow diffusion pumps to cool for a few hours before bringing up to atmosphere.

(c) close nupro "sample" valve.

(d) open glass valves above rubber hoses joining mechanical pumps to glassware, to admit air to glassware system.

(e) make repairs and follow startup procedures to obtain

vacuum again.

B.5 Zeroing Procedures

1. Cary Vibrating Reed Electrometers

Zero Procedure Check

- (a) place electrometer in "INPUT SHORTED" position.
- (b) turn on to " -ve CHARGE".
- (c) dial setting to "30 V".
- (d) warmup period 30 minutes.
- (e) zero electrometers by reducing scale by 1 factor and adjusting coarse and then fine tuning knobs, then drop to next scale.
- (f) end on "1 mV" scale.
- (g) make sure "damping" switch on preamplifier is off.

This is a preliminary test to make sure electrometers are functioning properly.

2. Daily Zeroing Procedures for Electrometers

- (a) turn on filament (should actually be on 30 minutes).
- (b) high voltage should also be turned on.
- (c) with no sample in system place switch on electrometers in "on" position or from "input" shorted position.
- (d) move dial to " + current".
- (e) zero as in (e) above.
- (f) note that zeroing should take place using appropriate resistor setting, i.e. , Resistor No. 1 - $10^8 \Omega$ - for hydrogen beam (Electrometer 2); Resistor No. 2 - $10^{10} \Omega$ for HD beam (Electrometer 1).
- (g) place electrometers on scales to be used normally

Electrometer 2 on 1 volt scale

Electrometer 1 on 100 mV scale

3. Calibrating Voltage-to-frequency converter

(a) leave in "on" position for 30 minutes to warm up electronics.

(b) move function switch to "calibrate converter".

(c) move the following switches on digital voltmeter

1. from "VOLT" to "FREQ"

2. from "CHECK" to "ATTENUATION"

(d) move switch on converter from "1 volt" to " + check".

(e) the number next to " + check" should be displayed on digital voltmeter, if not, use adjusting screw on " + cal" to obtain value. If difference is too great to be made with this adjusting screw, there is a coarse screw on the top of the converter that can be found by sliding converter part way out of rack.

(f) move switch on converter to " - check" from " + check".

(g) use same procedure as (e), but turning " - cal" adjusting screw.

B.6 Peak Scanning Procedure

(a) necessary after

(1) the filament has been replaced.

(2) modification to the source.

(3) major movement of the source.

(b) set up wiring for scanning on high voltage supply as depicted in Figure 4.9b - floating high potential. Do not touch machine ground when turning switches on or off.

(c) use startup and procedure for gas sampling, i.e.

Section B.2.

(d) use strip chart recorder to trace peak shapes.

(e) if peaks are not flat after initial scanning the analyzer magnet must be moved around by trial and error to obtain best peak shape.

(f) once magnet is in optimum position, adjust voltages on source plates using voltage divider resistances to further improve the peak shapes. Again, a trial and error procedure must be followed.

(g) once the peak shapes are satisfactory, then can obtain the voltage at which both peaks are simultaneously collected. Stop the scanning procedure and disconnect the scan electronics.

B.7 Corrective Procedures for Breakdowns in Equipment

1. Vacuum Problems

Poor vacuum is generally caused by leaks in the glassware. An indication of leaks in the system is the deep red to purple colouring within the glassware when a tesla coil is held close to the outside surface of the glassware. Generally leaks result only from the movement of the equipment or the breakage through some fault of the operator.

Here is a list of causes of poor vacuum in an order in which they generally occur:

- (a) Pin holes in glassware
- (b) Leaking stopcocks
- (c) Poorly fitting hoses
- (d) Fittings loose
- (e) Metal leak
- (f) Diffusion pumps not working
- (g) Ion pump not working

Some procedures to follow when repairing vacuum system are:

(a) Open system to atmosphere once pin hole leaks have been found by tesla coil (arcing of spark from leak to coil) and fix by glassblowing.

(b) If no pin hole leaks can be found in glassware using tesla coil, shut glass valves that are located between the diffusion pumps and the rubber hose leading to the mechanical pumps and check with tesla coil. If colour does not subside, turn exit stopcocks, i.e., vents to atmosphere in their sockets to regrease and reseal. Recheck with tesla coil. If this problem still persists do same to

the three-way stopcocks on sample inlet lines.

(c) If (b) has still no effect on leak, make sure hose is on properly, fitting well over the mechanical vacuum pump opening. Check with tesla coil. If there is no effect cut off two to three inches of hose and reclamp to vacuum pump. If still no effect on leak, make sure expiry date for oil change is not overdue.

(d) Vibrations from the mechanical vacuum pumps transmitted through the hose may have loosened Swedglock kovar seals. These can be checked using methanol or acetone sprayed on the fittings. If there is a leak at any of these points the colouring due to tesla coil will be deep red to purple.

Caution: Keep tesla coil away from sprayed liquid - fire hazard.

(e) This method also applies to metal leaks, gaskets, welds, etc. The methanol or acetone should only be applied with the mechanical pumps on. The diffusion pumps and ion pump should be shut off, and there should be no liquid nitrogen in the traps.

(f) If the ion gauge shows a low vacuum, then the diffusion pumps should be carefully felt by hand to check that there is heat to boil the mercury, if there is no heat, check the rheostat to make sure it is not shorted and then check the heater by measuring for a resistance. The voltage applied to these diffusion heaters should not exceed 80-85 volts.

(g) Again, if the ion gauge shows a fairly low vacuum, close the bellows valve and note the change in the vacuum gauge. No change indicates the ion pump may be worn out and needs replacing. A change indicates ion pump is good and that leak is elsewhere in the system. By opening the valve and then closing the "Nupro" valve

on gas sample inlet line will isolate the mass analyzer from the glassware and if the vacuum continues to improve, can concentrate efforts on glassware system to find leak.

2. Electronic Problems

Most electrical problems with the instrument will first be noticed by the rapid erratic fluctuations of the output signal of the electrometers. This indicates

- (a) Electrometer breakdown
- (b) Emission regulator breakdown
- (c) High voltage breakdown
- (d) Voltage divider breakdown

If both signals are behaving erratically, then the electrometers are probably all right. If only one signal is behaving in an odd manner, interchange the preamplifier cables. If the noise is transferred to the other electrometer, then the preamplifier will have to be checked. If noise does not, then original electrometer must be checked. These instruments, being of high precision should only be looked at by qualified technicians. Turn off High Voltage.

If both electrometers are behaving erratically simultaneously, then the emission regulator should be looked over. The filament and trap currents should be moving noticeably. Shut off regulator, disconnect from power source, i.e. cord to 120 VAC has to be pulled. Remove "Control" circuitboard and substitute spare one. Reconnect to power and turn back on, if signal still persists, shut off, disconnect power and replace "Power" circuit board. Reconnect to power source and turn on. If the trap current is stable once again, the problem has been located and the circuit boards will have to be

fixed, checking each component separately.

If erratic signals still persist, then the high voltage supply will then have to be investigated by plugging the output through the 10X voltage divider (do not exceed 3000 VDC on high voltage external scale) to the Hewlett Packard digital voltmeter and printer using one of the lines normally joined to the electrometer (make sure electrometer disconnected from digital equipment). Print out a few numbers -- if erratic pattern exists, high voltage supply will have to be checked out in electronics shop.

Finally, if erratic signal still persists then the voltage divider will have to be checked by placing high potential to it in the normal manner and placing a milli-ammeter in series between the ground of the voltage divider and the high voltage supply ground. Here, if there is any erratic noise, the current will move around. If not, the circuitry on the emission regulator not covered by the replacement of the printed circuit boards will have to be looked over in the electronics department. If the current on the ammeter is behaving erratically, then there is one or more faulty resistors on the voltage divider. Each resistor can be checked simply by shorting it out of the circuit by placing a wire in parallel with the resistor. Remember to shut off high voltage before jumping these resistors. Eventually, the erratic current will disappear and the faulty resistor can be removed and replaced.

3. Filament Failure

Noticable by no filament current when emission regulator turned on

(a) Shutdown electronic hardware.

(b) Check filament resistance after disconnecting lead if infinity, filament has to be replaced.

(c) If not, then check over emission regulator.

(d) Shut metal "Nupro" valve on sample inlet.

(e) Shut all-metal bellows valve to ion pump.

(f) Remove head flange from source using 7/16" socket.

(g) Disconnect filament leads on inside cables.

(h) Remove complete filament housing by undoing two hexhead bolts on case housing (place **tissue paper** in opening to ion pump to prevent anything going down tube).

(i) Take filament and its housing to mass spectrometer room in Physics building where they have arc welder and replace tungsten ribbon.

(j) Replace filament housing after first checking to make sure ribbon square with slit on housing.

(k) Reconnect filament leads and replace used gasket - clean with acetone first.

(l) Tighten flange using inch pound torque wrench set to maximum 140 in lbs.

(m) Open "nupro" valve on sample line very gradually.

(n) Wait a few hours then open bellows valve.

(o) Then proceed with filament backout as described in startup procedure.

B.8 Maintenance Requirements

The major requirements for the successful operation of the mass spectrometer can be broken down into daily, quarterly, and yearly maintenance schedules.

(a) Daily Maintenance

- the liquid nitrogen traps must be filled at 8(eight) hour intervals (prevents mercury from condensing in source),
- turning on and off the electronic equipment in the proper sequence.

(b) Quarterly (3 month) Maintenance

- shut the instrument completely down, letting mercury diffusion pumps cool for a few hours before bringing up to atmosphere, remove the nitrogen traps,
- remove the mercury from the traps using the ports provided and place in the heaters of the mercury diffusion pumps,
- remove all glass stopcocks, clean with KOH, lightly grease, and reinsert.

(c) Yearly Maintenance

- overhaul mechanical vacuum pumps, refill with clean oil,
- check rubber hoses for deterioration.

APPENDIX C
ISOTOPE RESULTS

C.1 Isotope Effects

Failure of early attempts to separate isotopes by chemical means lead to the belief that isotopes of an element were chemically similar. This concept was abandoned with the discovery of deuterium. Rittenburg and Urey (68) showed from statistical mechanics that for the reaction



the equilibrium constants were different from unity of different temperatures indicating differences in chemical behavior of the hydrogen isotopes. Farkas and Farkas (16) made similar studies for hydrogen-water exchange which they confirmed by experimental results. Since then calculations of equilibrium constants have been extended to many other isotope reactions (69).

With the detection of deuterium, experiments carried out by investigators demonstrated the existence of kinetic isotope effects, where the isotopic atoms and molecules react at different rates in competitive isotopic reactions. An example of this effect is the electrolysis of water, which grows richer in deuterium with time, a process which was first used to separate the isotopes (70). There has been an increase in interest in theory of kinetic isotope effects and their use in understanding reaction mechanisms.

Stable isotopes of numerous elements have been found to vary in their natural abundances. Natural isotope fractionation processes can be placed into two main categories:

- i) production of stable isotopes through radioactive decay of unstable nuclei

ii) variations resulting from mass dependent processes.

Numerous authors (10,12,71,72,73) have studied the cycle of water in the earth's atmosphere. The fractionation effect caused by vapour pressure differences of the isotopic species has resulted in an accumulation of the heavier isotopes in the equatorial regions. Geophysical investigations using the presence of two isotopic pairs, i.e., hydrogen and oxygen have revealed some important findings. Friedman (11) noted deuterium and oxygen 18 concentrations vary parallelly in sea water. The oceans have a uniform isotopic composition, disregarding areas mixed with fresh water, Epstein and Mayeda (73). Dansgaard (79) noted that variations in deuterium and oxygen 18 for precipitation processes follow the Rayleigh conditions. Thermal waters fractionate at different rates for deuterium and oxygen 18 (Craig (74)).

C.2 Laboratory Studies on Water Isotopes

There have also been work done at the laboratory level to study the mechanisms involved in evaporation processes. Draig, Boats and White (75) found that the kinetic effects in fast evaporation can disturb the above mentioned parallelism between deuterium and oxygen 18 variations. Further work by Craig, Gordon and Horibe (76) showed that deuterium and oxygen 18 concentrations of evaporating water into surroundings did not follow the Rayleigh batch distillation equation indicating that the reaction did not take place under equilibrium conditions.

If work is carried out at normal isotopic levels two important advantages become evident in the analysis. First, problems of synthesizing labelled compounds is avoided and second, errors of

contamination are minimized. Evaporation studies carried on by Bakr (77) were done using distilled tapwater in shallow basins. The oxygen 18 fractionation studies were made to determine the effect of these layers of hydrocarbons covering the evaporating surface. He noted that the films retarded the evaporation of water and lead to the increase in fractionation of the isotope of oxygen.

The work in this appendix is based on a set of samples from Bakr's studies to show the value of the mass spectrometer that was built for hydrogen isotope studies. The results of the oxygen 18 and deuterium enrichments are given in Table D-1, along with the experimental data supplied by Bakr. The data is presented in Figure C.1 to show the effects of the film on deuterium enrichment.

C.3 Calibration Procedure

It is much easier to measure relative or absolute differences between two samples than to measure the absolute value of the sample under study. The variations in isotopic compositions have created the greatest interest, and the measurement is consequently a common feature of all techniques previously applied in this field.

All data in this work will be given as the relative deviation, δ , of the heavy isotope content of a sample from that of a standard. If R is the isotopic ratio and R' is the isotopic ratio of the standard, both corrected for H_3^+ contributions, then δ will be considered as

$$\delta = \left(\frac{R - R'}{R'} \right) 10^3 = \left(\frac{R}{R'} - 1 \right) 10^3 \quad C.3.1$$

TABLE C-1
EXPERIMENTAL VALUES

	Sample No.	% Evap.	Hrs.	Measured $\delta^{18}\text{O}/^{16}\text{O}$	Measured δD
Without film	6B1	24	48	4	15
	6B2	45	89	8	48
	6B3	58	116	13	72
	6B4	73	144	17	105
	6B5	92.5	190	26	165
	6B6	98.5	217.5	31	204
2.44×10^{-4} cm film	6A1	17	71	2	18
	6A2	37	144	7	51
	6A3	58	217.5	15	93
	6A4	76	281	20	128
	6A5	91	331	29	180
	6A6	99.4	354	34	215
1.00×10^{-3} cm film	6C1	18	92	3	11
	6C2	38	169	7	54
	6C3	61.5	281	16	102
	6C4	77	331	22	144
	6C5	90	379	33	200
	6C6	99.5	402.5	38	-
2.44×10^{-3} cm film	6D1	18.5	116	3	27
	6D2	36	190	7	60
	6D3	63	310.5	17	120
	6D4	78	379	24	147
	6D5	92	429	34	195
	6D6	99	439	36	217

The reference standard is Standard Mean Ocean Water, SMOW Craig (74), which is an artificial standard in terms of the National Bureau of Standards reference I. such that

$$(D/H)_{SMOW} = 1.050(D/H)_{NBS-1} \quad C.3.2$$

Isotopic data is reported as per mil enrichments, δ , or depletions relative to SMOW so that data from around the world can be easily compared. There has been a double method of reporting deuterium, i.e., as per mil, or as atomic parts per million (ppma).

These can be interchanged quite readily, but the problem of obtaining the absolute value is indeed a very difficult one, since the mass spectrometer has to be calibrated with samples that contain very pure hydrogen standards, ones that are not readily available to most laboratories. Therefore, it is much easier to give the per mil deviations from SMOW than to obtain precise absolute value for the sample.

C.4 Results

The results shown in Figure C.1 indicate that as the thickness of the film increases, deuterium appears to increase in the remaining water. These figures coincided with results of the study of the enrichment of oxygen 18 done on the same samples (77). It can be noted, however, that the deuterium content of evaporating waters appeared to approach the same final value. This can partly be explained by the way the samples were handled and stored. The analysis of the samples made available for deuterium study were in glass sample jars with a plastic stopper. The deuterium of the very high enriched samples could have possibly exchanged with the surrounding

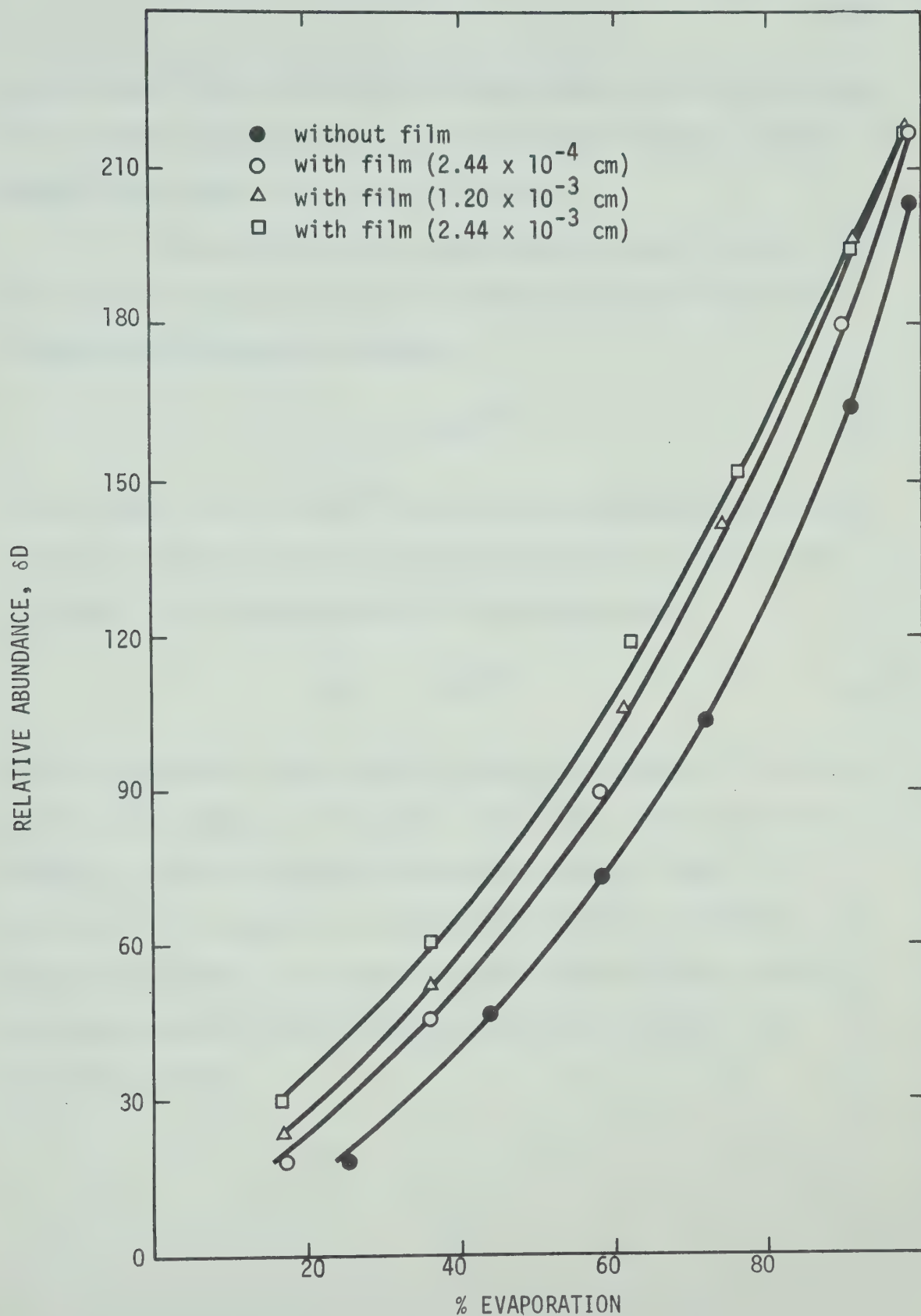


Figure C.1 EFFECT OF FILM THICKNESS ON ENRICHMENT OF DEUTERIUM

water vapour in the air by the diffusion around the unsealed stopper. This is quite feasible since a year had elapsed from the time the samples were taken until they were analyzed.

Previously Craig (74) found that for natural waters, the fractionation of oxygen 18 and deuterium appeared to follow the relationship for natural abundances.

$$\delta D \approx 8 \delta O^{18} \quad C.4.1$$

In this work, the δD and δO^{18} values for the samples were obtained and the relationship shown for the water without a film was given in Figure C.2. The relationship of the isotopes was

$$\delta D \approx 6.5 \delta O^{18} \quad C.4.2$$

This is higher than that found for evaporating waters, i.e., slope of 5.5. The slopes for the waters with films of them increased slightly, with the thickest film having a slope of $\delta D/\delta O^{18}$ of 7. The use of films appears to increase the isotope of hydrogen in the evaporating waters as the film increases and the thicker the film, the more apparent is this effect on the fractionation of the deuterium isotope.

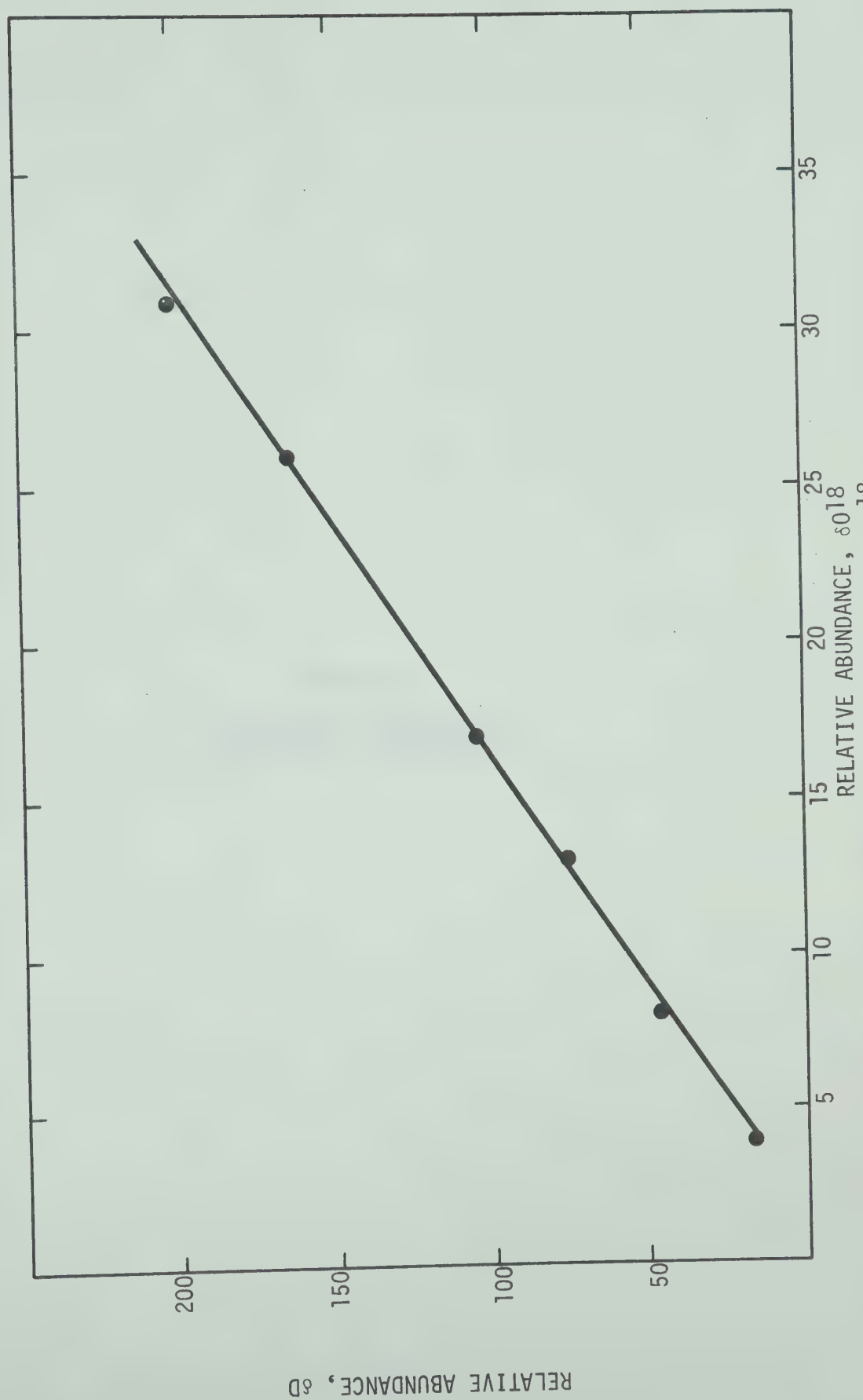


Figure C.2 RELATIVE AMOUNTS OF DEUTERIUM, OXYGEN 18 IN EVAPORATING WATER WITHOUT A FILM

APPENDIX D
GAS SAMPLE PREPARATIONS

Deuterium concentration in natural water is commonly given as parts per million of heavy water, that is, on a molecular basis

$$\frac{D_2O}{H_2O + D_2O} \times 10^6 \quad D.1$$

Deuterium, though, is present almost entirely as HDO at the natural concentration levels. At natural level, water is essentially equivalent to the atom ratio $D/H \times 10^6$. In the enrichment of natural water it is essential to know the value of deuterium content of this water. In this case, Edmonton tapwater that has been distilled and demineralized is used and has a value of 130.5 ppma (67).

Enriched water was made up by addition of reactor grade heavy water 99.87% D_2O to this natural water. Since it requires 2 atoms of deuterium to make one mole of heavy water and similarly for hydrogen to make natural water, then their atom and mole fractions are equivalent.

D.1 Gas Samples

To make gas samples, once the water sample has been prepared, it is introduced into a Milton Roy Hygler hydrogen generator. This is essentially an electrolysis machine that allows for the build-up of ultra pure hydrogen to pressures of 400 psig. The separation factor for the exchange of hydrogen gas containing deuterium with the water containing deuterium has a value of approximately 5. Therefore the liquid must contain five times the amount of deuterium required in the gas.

The formula used to obtain the necessary amount of heavy water that has to be added to the Edmonton water can be derived and

only the final form is shown here.

$$X = \frac{W_T B}{1 - C_2} (C_2 - C_1) \quad \text{D.1.1}$$

where

X [=] amount of heavy water to be added, gm

W_T [=] weight of Edmonton tap water used, gm

B [=] ratio of molecular weights of heavy water/
ordinary water = 1.1110

C_1 [=] concentration in ppma of tap water

C_2 [=] concentration in ppma that is required

for example, want hydrogen gas with 200 ppma deuterium, then require liquid with 1000 ppma (separation factor = 5).

Then, if have 500 gm of Edmonton tapwater, the amount of heavy water that must be added is 0.484 gm.

D.2 Procedure for Obtaining Gas Sample

1. weigh out amount of natural water to be used
2. specify concentrations required and use equation D.1.1 to obtain weight of heavy water to be added
3. use micro litre syringe to weigh out required amount
4. mix liquids thoroughly, place in airtight container
5. introduce to hydrogen generator, let gas be vented
6. introduce a second batch of same material to generator, collecting gas this time in gas bombs used for analysis on mass spectrometer.

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